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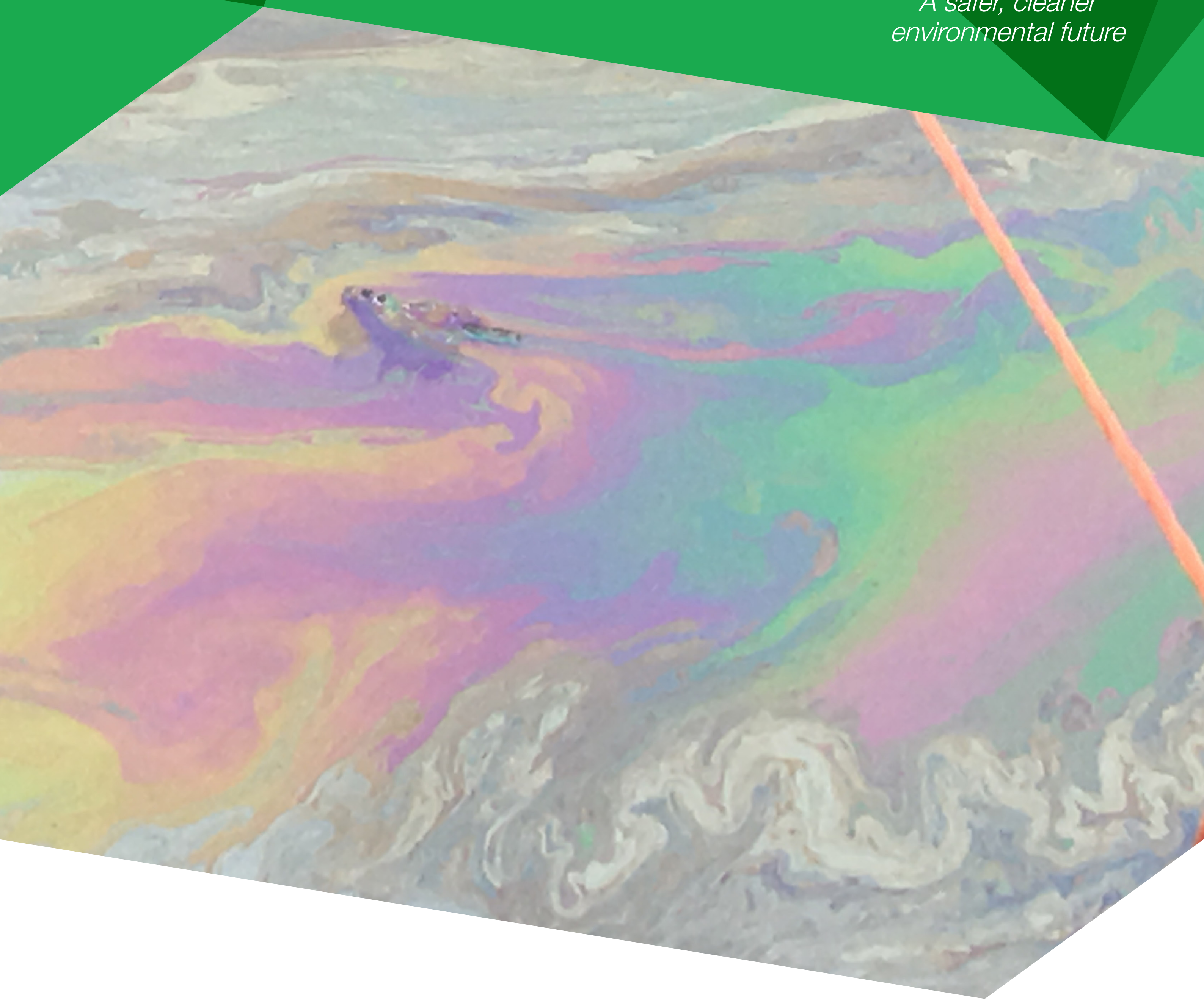

TECHNICAL REPORT NO. 46

The role of natural source zone depletion in the management of light non-aqueous phase liquid (LNAPL) contaminated sites

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CRC for Contamination Assessment and Remediation of the Environment

Technical Report no. 46

The role of natural source zone depletion in the management of light non-aqueous phase liquid (LNAPL) contaminated sites

February 2020

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Executive summary

The consideration of the role of natural biodegradation in the management of petroleum-contaminated sites is not new. It has been well-established for some time that dissolved and vapour phase petroleum hydrocarbons readily biodegrade in the subsurface at light non-aqueous phase liquid (LNAPL) sites. However, there is a growing understanding of the natural processes involved in the depletion and degradation of the LNAPL itself (collectively referred to as natural source zone depletion (NSZD)). While practitioners have undoubtedly seen countless LNAPL fingerprinting reports indicating LNAPLs were degraded to various degrees over the years, the potential significance of NSZD rates and our understanding of where and how we should look to quantify NSZD has only become apparent more recently. CRC CARE Technical Report 44, *Technical measurement guidance for LNAPL natural source zone depletion* was published in August 2018 in order to provide guidance on, and standardisation of methodologies for the emerging practice of monitoring NSZD at LNAPL sites in Australia. While Technical Report 44 focused specifically on NSZD measurement methodologies, this report takes a broader view in order to support regulators and practitioners in identifying the different ways the role of NSZD may be considered in the overall management of LNAPL sites.

This report discusses a growing body of research showing that NSZD is ubiquitous at LNAPL sites. NSZD processes occur at all LNAPL sites to some degree and understanding, quantifying and evaluating their effectiveness is therefore an important part of a sustainable remedial strategy (CL:AIRE 2019). Accordingly, the potential significance of NSZD at Australian sites has implications with respect to the development of LNAPL conceptual site models (LCSMs) and remedial/management strategies. The assessment of NSZD and use of NSZD data can be considered at different points in LNAPL site management including:

- **During the development of the LCSM** as a baseline evaluation of LNAPL degradation and to better understand and support conclusions regarding LNAPL stability.
- **During the assessment of remedial/management options** as a component of a remedial/management strategy and/or to better understand the incremental benefits of other remedial options such as active LNAPL recovery compared with NSZD alone.
- **During the implementation of the remediation/management strategy** as a primary LNAPL management technique, as a secondary approach following active recovery methods, and/or as a consideration when assessing whether an acceptable endpoint to active remediation has been reached. Since NSZD is a ubiquitous, naturally occurring phenomenon, it will be part of all LNAPL site management strategies. As a standalone remedy, NSZD will be most applicable where LNAPL is stable, LNAPL recovery is technically infeasible and/or will not provide a technical benefit, and there are no unacceptable human health or environmental exposures (or exposures can be effectively mitigated with controls).

Case studies are presented that provide a number of insights regarding NSZD in general and NSZD at Australian sites specifically. The case studies add to the growing body of evidence that NSZD rates observed at Australian sites are comparable or exceed what is considered typical overseas. Additionally, the case studies indicate that NSZD was found to be substantially outperforming conventional active LNAPL recovery performance at all sites where the comparison was possible (i.e. where active LNAPL recovery efforts were taking place).

The study of NSZD is an area of active research, particularly with respect to the refinement of best practices in monitoring methodologies and longer-term studies that will facilitate the assessment of NSZD rate trends over time and the development of predictive modelling applications. In an attempt to address these needs, ongoing studies at Australian sites by CSIRO using multiple monitoring methodologies concurrently with different LNAPL types in different settings are underway.

This document focuses solely on technical considerations and does not provide specific guidance on the applicable regulatory frameworks in the different Australian jurisdictions. Any proposed remedial/management strategy must first consider the specific regulatory requirements related to the protection of human health and the environment. Early consultation with regulators is recommended to confirm that the intended use of NSZD will be acceptable.

Abbreviations

API	American Petroleum Institute
AS/SVE	Air sparge/soil vapour extraction
ASTM	ASTM International
BTEX	Benzene, toluene, ethylbenzene and xylenes (collectively)
CH_4	Methane
CL:AIRE	Contaminated Land: Applications in Real Environments
CO_2	Carbon dioxide
CO_{2e}	Carbon dioxide equivalents
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSM	Conceptual site model
C_{sat}	Threshold bulk soil concentration, which when exceeded, indicates that a non-aqueous NAPL phase is likely to be present in the soil matrix.
DCC	Dynamic closed chamber
ft^2/day	Feet squared per day
FID	Flame ionisation detector
HERA	Health and ecological risk assessment
ITRC	Interstate Technology & Regulatory Council
kg/m^3	Kilograms per cubic metre
kL	Kilolitres
$L\ ha^{-1}\ yr^{-1}$	Litres per hectare per year
$L\ yr^{-1}$	Litres per year
LIF	Laser-induced fluorescence
LNAPL	Light non-aqueous phase liquid
LCSM	LNAPL conceptual site model
m^2/day	Metres squared per day
mg/kg	Milligrams per kilogram
mg/L	Milligrams per litre
mm	Millimetre

MNA	Monitored natural attenuation
MPE	High-vacuum multi-phase extraction
N_2O	Nitrous oxide
NO_x	Oxides of nitrogen
NEPM	National Environment Protection Measure
NERA	National Energy Resources Australia
NSZD	Natural source zone depletion
O_2	Oxygen
PID	Photoionisation detector
PVI	Petroleum vapour intrusion
S_o	LNAPL/oil saturation
SEFA	Spreadsheets for environmental footprint analysis
SO_x	Oxides of sulphur
S_r	Residual LNAPL saturation
T_n	LNAPL transmissivity
t yr^{-1}	Tonnes per year
TPH	Total petroleum hydrocarbons
USA	United States of America
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compound

Glossary

Capillary pressure	The pressure difference between the non-wetting phase (i.e. LNAPL) and the wetting phase (i.e. groundwater) in a multiphase system such as an LNAPL-groundwater system.
Conceptual site model (CSM)	The overall aim of the CSM, which, from the perspective of contaminated sites management is integral to the process of risk assessment, is to enable source–pathway–receptor relationships to be assessed to support the evaluation of the significance of plausible pollutant linkages. All three elements must be present for harm to be realised, triggering the requirement for further investigation, additional risk assessment or remediation.
Effective solubility	The solubility of an individual compound (e.g. benzene) that will dissolve from a chemical mixture (e.g. petrol) into water. Effective solubility is usually significantly less than the compound's pure phase solubility. Effective solubility is described by Raoult's Law, which indicates that the solubility limit of any individual component of a complex mixture will be limited by the simultaneous dissolution of the other components of the mixture and will be equal to a component's pure phase solubility multiplied by the mole fraction of the component in the mixture.
Ganglia (LNAPL)	Isolated disconnected globules of LNAPL trapped within pore spaces. Under natural conditions, they are likely to remain as immobile residual that cannot be practically removed.
Intergenerational equity	A concept that says that humans hold the environment of the Earth in common with other members of the present generation and with other generations past and future, implying an obligation to pass the environment in reasonable condition to future generations. In this report, intergenerational equity additionally considers the environmental footprint of remedial systems, particularly as they may relate to climate change.
In-well LNAPL thickness	The observed thickness of LNAPL in a monitoring well, which relates to the pressure and spatial distribution of LNAPL in the subsurface. In-well LNAPL thicknesses in monitoring wells vary with changes in groundwater elevations and will often not correlate with LNAPL mobility or recoverability. In-well LNAPL thickness is therefore considered a poor threshold or end-point metric for hydraulic LNAPL mass recovery.

Light non-aqueous phase liquid (LNAPL)	An organic or inorganic liquid that is not miscible with water and has a specific gravity less than 1.0 (e.g. petrol, diesel).
LNAPL compositional change	Application of a technology that indirectly remediates the LNAPL body via recovery and/or in-situ destruction or degradation of vapour or dissolved-phase LNAPL constituents.
LNAPL conceptual site model (LCSM)	Extension of the conventional hydrogeological CSM to include LNAPL-specific properties and parameters, such as intrinsic permeability, relative permeability and LNAPL transmissivity.
LNAPL gradient	The LNAPL gradient is generated by the head of the release and dissipates over time until it approximately matches the hydraulic gradient. The LNAPL gradient is calculated with reference to the top of LNAPL in wells. An LNAPL gradient is necessary for LNAPL migration/ expansion to occur independent of LNAPL saturation levels.
LNAPL saturation (S_o)	The LNAPL-filled fraction of the total porosity (e.g. 0.1 or 10% LNAPL saturation indicates that 10 percent of the total porosity is filled with LNAPL).
LNAPL smear zone	The zone within the upper portion of the saturated zone and the lower portion of the vadose zone containing LNAPL at variable saturation, where the mobile fraction undergoes periodic/localised redistribution in response to water table fluctuations.
LNAPL management	A process that includes LNAPL site assessment and monitoring, LNAPL conceptual site model development, identification and validation of LNAPL concerns, and application of remediation technologies, if needed to address any LNAPL concerns.
LNAPL mass recovery	Application of a technology that physically removes LNAPL without significant reliance on compositional/ phase change. Most often refers to hydraulic LNAPL recovery methods.

Mobile LNAPL	LNAPL mobility refers to the movement of LNAPL on a localised scale at some point within an LNAPL body. Mobile LNAPL refers to LNAPL that exists above residual saturation levels such that it may be observed in wells. Mobile LNAPL has the potential to migrate, but not all mobile LNAPL contributes to LNAPL body expansion/ migration. Once an LNAPL body becomes stable, the observation of mobile LNAPL in wells typically will not indicate that a significant fraction of the LNAPL in the adjacent subsurface is recoverable or that there is potential for LNAPL body migration.
Mole fraction	The amount of a given constituent in moles divided by the total amount of moles (summation of all constituents) in a mixture or solution.
Monitored natural attenuation (MNA)	Natural attenuation is the combination of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. In the context of petroleum releases, MNA typically focuses on the documentation of the attenuation of petroleum constituents in the dissolved phase via monitoring over some duration of time.
Natural attenuation	The combination of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. In the context of petroleum releases, MNA typically focuses on the attenuation of petroleum constituents in the dissolved phase, in contrast to NSZD, which focuses on the depletion of mass within the LNAPL source zone.
Natural source zone depletion (NSZD)	The combined action of natural processes that reduce the mass of LNAPL in the subsurface. Key processes include volatilisation, dissolution, and biodegradation. Over time, depletion of LNAPL mass will reduce LNAPL saturation/mobility and result in LNAPL phase/ compositional change.

LNAPL recoverability	LNAPL recoverability is a measure of the mobility of the LNAPL for comparison against some criterion above which LNAPL mass recovery might be considered practicable. Therefore, recoverable LNAPL can be thought of as LNAPL that has a certain degree of mobility. Potential hydraulic recoverability reflects the volume of LNAPL above residual saturation; however, due to inherent inefficiencies in extraction, recoverability typically reaches near zero values before residual saturations are attained. Commonly quantified in terms of LNAPL transmissivity.
LNAPL remediation	Application of an LNAPL mass recovery, phase/ compositional change and/or source reduction technology to achieve a defined remediation objective.
LNAPL transmissivity (T_n)	LNAPL transmissivity is a proportionality coefficient that describes the ability of a porous media to transmit a specific LNAPL and is defined as the volume of LNAPL that may pass through a unit width of aquifer per unit time per unit gradient. It is a measure of the potential for LNAPL to flow and thus its potential recoverability.
Remedial endpoint (LNAPL)	A realistic, achievable, measurable and agreed-upon LNAPL remedial technology-specific point at which active treatment can be terminated. The LNAPL end point is often based on declining recovery rates or asymptotic LNAPL recovery curves. In essence, the limit of practical LNAPL remediation of a particular technology that takes account of the inherent limits of the system.
Remedial objective (LNAPL)	The LNAPL condition to be achieved by the remedial strategy or action that constitutes the desired or aspirational outcome of remediation.
Residual LNAPL	The fraction of an LNAPL body that will remain immobile and hydraulically unrecoverable under prevailing hydraulic conditions (i.e. will not flow into a well).
Residual LNAPL saturation (S_r)	The saturation at and below which LNAPL will no longer flow in an aquifer even under applied gradients. Residual LNAPL is immobile/unrecoverable and therefore does not contribute to migration risk; however, it may continue to act as a source of dissolved and/or vapour phase contamination.

Site sensitivity	Site sensitivity in the context of this guidance relates to impact assessment – the potential risks that LNAPL poses to human health or sensitive terrestrial and aquatic ecology, and also to the economic value of the land, both in financial terms (e.g. real estate or productive value) and in terms of social and environmental values (e.g. amenity value).
Stable LNAPL	An LNAPL body that no longer possesses the potential to migrate or expand into areas previously un-impacted by LNAPL (i.e. a stable LNAPL body is not migrating). Stability is judged by time-series data and controlled by physical processes (capillary pressure and volatilisation) and biodegradation. LNAPL stability refers to the movement of LNAPL on a macro or LNAPL body-wide scale. The main difference between LNAPL stability and LNAPL mobility is therefore the frame of reference. Some level of mobile LNAPL that does not affect the overall stability of an LNAPL body can be, and typically is, present within a stable LNAPL body extent.
Stakeholder	A person, group or organisation that has an interest in the project, the derivation of the remedial objectives or the outcome of the remediation program. Stakeholders typically include state and territory regulators, site owners, site operators, contaminated site auditors (where applicable) and individuals within the environs of the site, including those who might be affected by the migration of contamination across a site boundary.
Sustainability	There are many definitions of sustainability. In the context of LNAPL remediation, sustainable refers to the principles of ecologically sustainable development, which is a provision in the contaminated sites legislation of several states and territories. Ecologically sustainable development principles include the concepts of intergenerational equity and the precautionary principle. Sustainability and economics assessments merge when the full life-cycle costs and benefits of each LNAPL remedial approach are considered. In this document, the assumption is made that active remedial approaches must result in a net environmental benefit to be considered sustainable.
Threshold metric	Measured data or site condition(s) that can indicate whether an initial LNAPL concern may be eliminated or carried forward to select remediation objectives.
Vadose zone	The unsaturated zone between the land surface and the groundwater table.

Wettability	The tendency of a fluid, based on surface tensions, in a multiphase system to preferentially coat or wet the solid phase of a soil or porous rock medium. Typically, water has a preference for small pore spaces, air for larger pore spaces and LNAPL for intermediate-sized pores. Water is therefore described as the wetting fluid, air as the non-wetting fluid and LNAPL as the intermediate wetting fluid.

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Acknowledgements

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1. Introduction

1.1 Background

As light non-aqueous phase liquid (LNAPL) science has progressed, relevant guidance has evolved over time to adopt an improved LNAPL site management approach through the application of science and risk-based principles. This evolution in LNAPL science and guidance is evident in previous CRC CARE technical reports that have addressed a number of topics relevant to the management of LNAPL sites including site characterisation, risk assessment, dissolved and vapour phase natural attenuation and remedial approaches.[1] In February 2015, CRC CARE published Technical Report 34, *A practitioner's guide for the analysis, management and remediation of LNAPL*. Since then, there have been additional advances in approaches for LNAPL site characterisation and management, most notably with respect to the growing awareness of the important role of natural processes in the depletion and degradation of LNAPL (collectively referred to as natural source zone depletion (NSZD)). In general, a consideration of the role of natural biodegradation in the management of petroleum-contaminated sites is not new. It has been well-established for some time that dissolved and vapour phase petroleum hydrocarbons readily biodegrade in the subsurface at LNAPL sites. As an illustration, dissolved phase natural attenuation (commonly referred to as monitored natural attenuation (MNA)) is generally viewed as an established remedial technique or endpoint. However, there have been significant advancements in our understanding of the natural processes involved in the depletion and degradation of the LNAPL body source material.

This new understanding represents an extension of our knowledge relating to the biodegradation of dissolved and vapour phase petroleum hydrocarbons to encompass the LNAPL body itself. While practitioners have undoubtedly seen countless LNAPL fingerprinting reports indicating LNAPLs were degraded to various degrees over the years, the potential significance of NSZD rates and our understanding of where and how we should look to quantify NSZD has only become apparent more recently. CRC CARE Technical Report 44, *Technical measurement guidance for LNAPL natural source zone depletion* was published in August 2018 in order to provide guidance on, and standardisation of, methodologies for the emerging practice of monitoring NSZD at LNAPL sites in Australia. While Technical Report 44 focused specifically on NSZD measurement methodologies, this report takes a broader view in order to assist regulators and practitioners in identifying the different ways the role of NSZD may be considered in the overall management of LNAPL sites.

1.2 Objective

The primary objective of this report is to provide a technical resource that can be used by Australian regulators, practitioners and site owners to support risk-based decision making and consider the different ways the role of NSZD may have implications in the overall management of LNAPL sites. In order to accomplish this objective, this report demonstrates how LNAPL site management decision making can be enhanced through the consideration and measurement of NSZD processes and other science-based

[1] *For example, see CRC CARE Technical Reports 2–4, 8–13, 15, 18, 23, 34, 40 and 44.*

metrics in the development of the LNAPL conceptual site model (LCSM) and the associated site management strategy. Ultimately, the goal is to demonstrate how the incorporation of NSZD into the LNAPL site management process can lead to better outcomes by providing a more realistic perspective on the potential benefit, practicability and sustainability of a given LNAPL site management approach.

1.3 Limitations

The following limitations are noted with respect to the technical guidance provided herein:

- The evaluation and monitoring of NSZD represents an area of active research and best practices involved in NSZD test methodologies and strategies for the integration of NSZD into LNAPL site management may evolve over time. For example, CSIRO continues to study a number of NSZD test sites where multiple monitoring approaches are being implemented concurrently in an effort to refine best practices in this area and develop longer-term data sets. In addition, CSIRO is continuing to evaluate modelling approaches that may be applicable to NSZD and the prediction of longer-term rate trends based on current monitoring (Sookhak Lari *et al* 2019).
- This document only focuses on technical considerations and does not provide specific guidance on the applicable regulatory frameworks in the different Australian jurisdictions. Any proposed remedial/management strategy must first consider the specific regulatory requirements related to the protection of human health and the environment as paramount. Early consultation with regulators is recommended to confirm that the intended use of NSZD will be acceptable.

2. LNAPL fundamentals

The intent of this section is to revisit LNAPL fundamentals by providing a brief overview of LNAPL body formation and longer-term changes in LNAPL bodies that will have an effect on-site management strategy. Revisiting concepts that relate to when LNAPL mobility may be a concern, when LNAPL mass recovery is likely to provide a benefit and exploring the role of NSZD in LNAPL site management will be of particular focus. CRC CARE Technical Reports 34 and 44 provide more detail on LNAPL and NSZD fundamentals. In addition, guidance from CL:AIRE (2014), the Interstate Technology & Regulatory Council (ITRC 2018) and American Petroleum Institute (API 2018) are considered to be primary resources for information on LNAPL fundamentals.

2.1 Initial LNAPL body formation dynamics

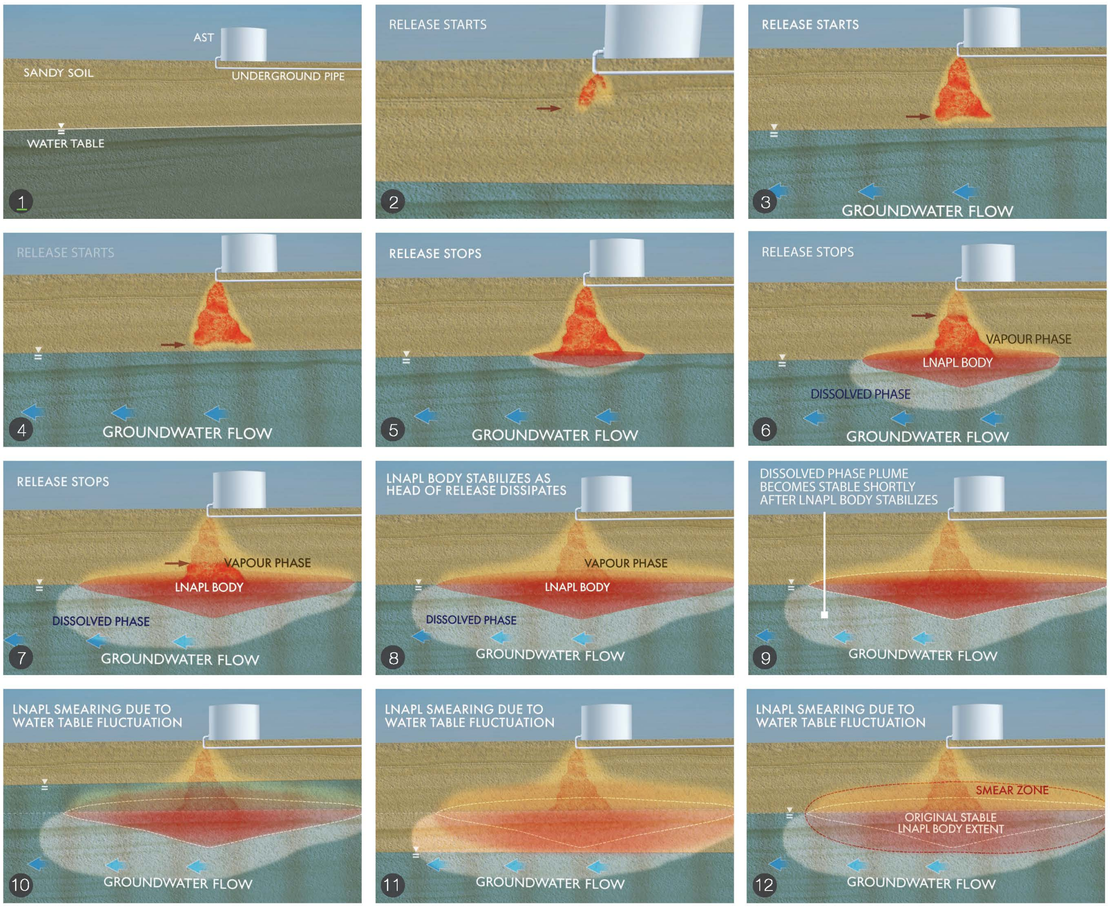

Figure 1: Conceptual LNAPL body formation (provided by GHD).

The conceptual formation of an LNAPL body in the subsurface is illustrated in Figure 1. The different stages of LNAPL body formation and stabilisation are described with reference to the frames shown in Figure 1.

2.1.1 Initial release stage

The initial release stage is represented in frames 1–4 in Figure 1. When released to the subsurface, LNAPL will move downward through the vadose zone under gravitational forces to some depth that will be proportional to the volume (LNAPL head or pressure) generated by the release. Lateral spreading experienced during this stage will be controlled by preferential pathways that may exist due to subsurface infrastructure or higher permeability features in the soil or rock matrix. If a release has insufficient volume/LNAPL head to reach the water table, the resulting LNAPL body would remain wholly within the vadose zone and would exist at predominantly residual levels of saturation (ASTM 2014; CL:AIRE 2014; CRC CARE 2015; ITRC 2018).[2,3]

2.1.2 Active migration/expansion stage

The active LNAPL migration/expansion stage is illustrated in frames 5–7 in Figure 1. If enough LNAPL volume is released, LNAPL will at some point reach the water table. The groundwater and resistive forces in the soil will inhibit further downward LNAPL movement until such time as the pressure generated by the LNAPL head that builds up is sufficient to push groundwater out of the surrounding pore space (referred to as critical head or pore entry displacement pressure). At this point, the LNAPL is able to enter previously groundwater-filled pore space by displacing some of the groundwater. The LNAPL will exist both above and below the water table with the amount of LNAPL within a given pore space (i.e. the LNAPL saturation) dependent on the pressure generated at that specific point by the release. Figure 2 provides a conceptualisation of a typical LNAPL saturation profile, showing significant proportions of the LNAPL volume present in both the vadose and saturated zones and peak saturation levels (i.e. the most potentially mobile LNAPL) just above the equilibrium water table elevation. As shown in Figure 3, the pore space will always retain some groundwater and will never be completely filled with LNAPL, with LNAPL saturation levels much less than 100% (of the pore space) typical at LNAPL sites (ASTM 2014; CL:AIRE 2014; CRC CARE 2015; ITRC 2018).

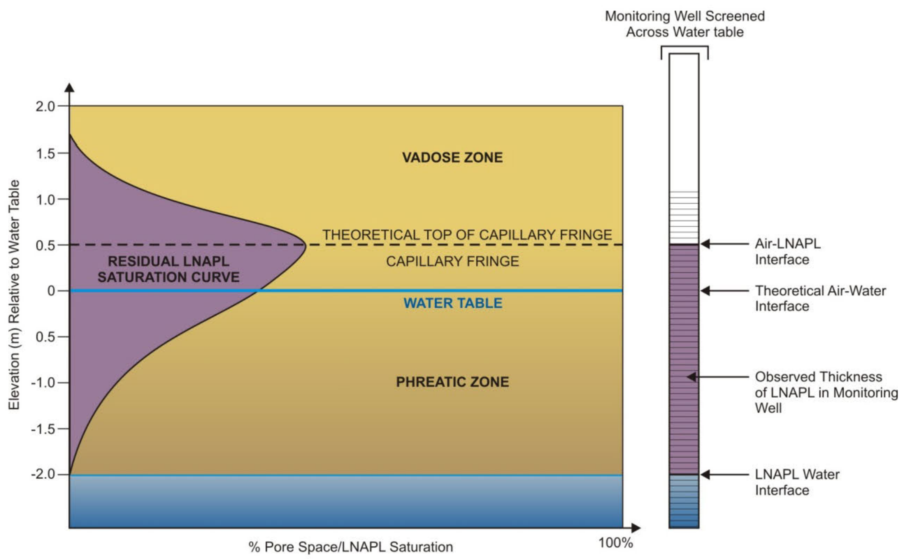

Figure 2: Idealised LNAPL saturation profile and corresponding well observation (CRC CARE 2015)

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[2] *LNAPL saturation: percent of the pore space filled with LNAPL*
[3] *Residual LNAPL saturation: saturation level below which LNAPL will largely exist in a discontinuous, hydraulically immobile and unrecoverable state*

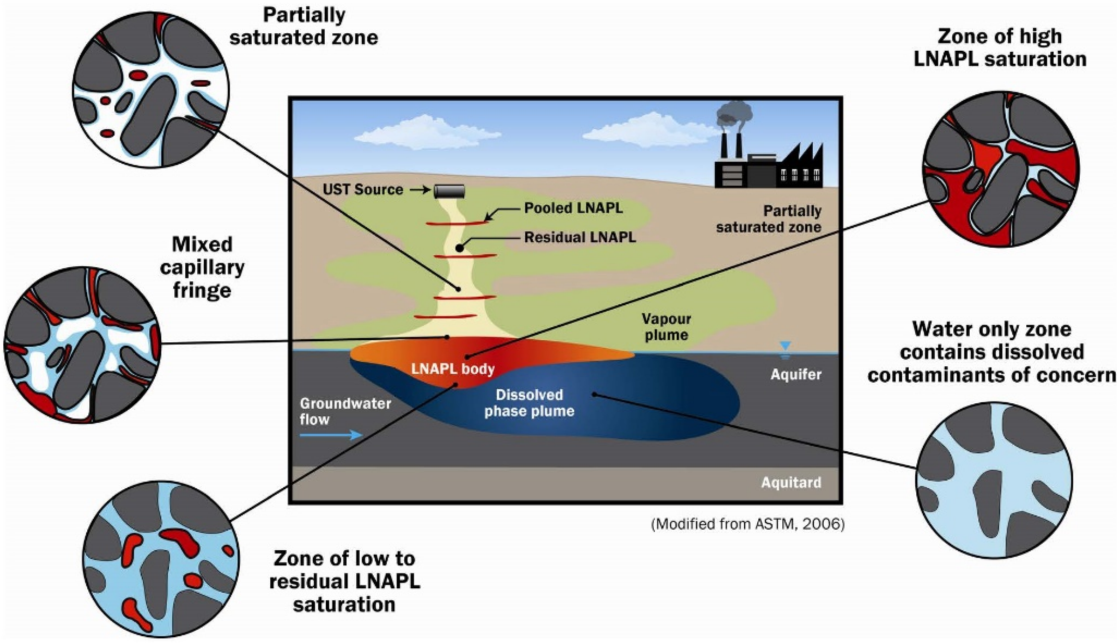

Figure 3: Conceptualisation of LNAPL saturation levels in different parts of an idealised LNAPL body showing a localised area of continuous elevated LNAPL saturation surrounded by LNAPL at predominantly low/residual saturation levels (from CL:AIRE 2014)

Lateral LNAPL movement in both the saturated zone and capillary fringe will be driven by the LNAPL head, with LNAPL spreading radially (up-gradient, cross-gradient, down-gradient) with preferential movement in the direction of the hydraulic gradient and along/through any natural or man-made preferential pathways. The displacement of groundwater by LNAPL (i.e. LNAPL spreading) in the pore space will continue as long as the LNAPL head exceeds the resistive forces in the subsurface. The fraction of the LNAPL body that might be mobile and hydraulically recoverable will be at its maximum during this initial stage of active migration/expansion.

The LNAPL head will dissipate following the cessation of a release on a timescale that can vary from days to years depending on the volume of the release, the LNAPL type, and subsurface conditions (CL:AIRE 2014; ITRC 2018; Sookhak Lari *et al* 2019). An LNAPL body consisting of a low viscosity LNAPL type such as petrol can be expected to stabilise on a timescale of weeks to months, whereas a more viscous LNAPL type such as heating oil might take months to years to stabilise (CL:AIRE 2014). Figure 4 provides a typical example where a fuel oil LNAPL was observed to largely achieve LNAPL body stabilisation (i.e. the maximum LNAPL body footprint) within one year of the original release.

Figure 4: LNAPL release of fuel oil observed in monitoring wells showing that LNAPL body stability was largely achieved in 1 year (API 2004)

An LNAPL body becomes stable when the LNAPL head is insufficient to allow the movement of LNAPL into areas that do not already contain LNAPL (CL:AIRE 2014; CRC CARE 2015; ITRC 2018). Within stable LNAPL bodies, localised areas containing mobile LNAPL (i.e. LNAPL that is sufficiently mobile to enter wells) will typically persist. This can be conceptualised as an LNAPL body with localised areas of higher LNAPL saturation surrounded by areas of lower/residual levels of saturation (Figure 3). The result is the common observance of LNAPL in wells that does not contribute to any migration or expansion of the larger overall LNAPL body extent (Huntley & Beckett 2002).

When an LNAPL release occurs in fractured rock, the distribution of LNAPL and time to stabilisation might be very different than in a porous media (i.e. soil) scenario. The behaviour of LNAPL in rock that is highly weathered or densely fractured may be very similar to what would be expected in a porous media. However, a rock matrix with a highly interconnected network of large aperture fractures may provide less resistance to LNAPL spreading initially, which could result in a larger LNAPL extent (both laterally and vertically) and a more complex LNAPL distribution. Conversely, a fracture network that is not highly interconnected may provide fewer pathways for LNAPL spreading than a given soil scenario, leading to a smaller LNAPL extent and shorter time to stabilisation (ITRC 2017). More detailed discussion of LNAPL behaviour in the fractured rock settings that are common in Australia is provided by CL:AIRE (2014) and ITRC (2017).

KEY POINTS:

1. **LNAPL bodies consist of continuously variable proportions of LNAPL, water and/or air coexisting in the pore space both above and below the water table (think iceberg, not pancake).**
2. **The pore space at LNAPL sites will never be 100% filled with LNAPL.**
3. **LNAPL bodies stabilise on a timescale that can vary from days to years depending on the volume of the release, the LNAPL type, and subsurface conditions.**

2.2 Constituent partitioning

As noted, LNAPL becomes part of a multiphase system where it is in contact with air, groundwater, and/or soil once released to the subsurface. This leads to the partitioning of LNAPL constituents into different phases, most notably the dissolved and vapour phases. Partitioning is therefore the primary mechanism whereby LNAPL constituents can move away from the LNAPL source zone in groundwater or soil gas where receptors may be exposed.

The concentration of a given LNAPL constituent in groundwater or soil gas will be proportional to the concentration (mole fraction) of the constituent in the LNAPL source material. Therefore, the concentrations of constituents in the dissolved and vapour phases are most sensitive to LNAPL composition, and relatively insensitive to LNAPL volume or saturation levels (ITRC 2018). As such, changes in LNAPL volume or saturation levels that do not alter LNAPL composition (i.e. source strength) will not result in a commensurate change in dissolved or vapour phase constituent concentrations. Where significant reductions in LNAPL volume/saturation occur, some reduction in the extent of a dissolved plume or vapour migration may also occur.

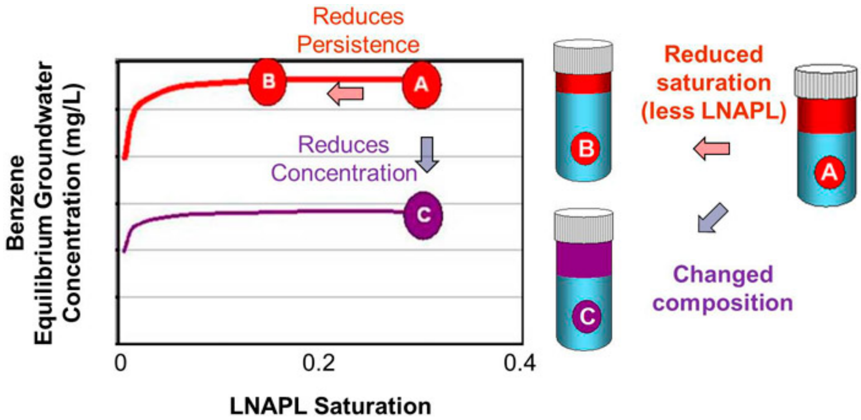

Figure 5: Conceptual effects of LNAPL saturation reduction (A→B) and LNAPL compositional change (A→C) on dissolved benzene concentration (from ITRC 2018)

The relationships between changes in LNAPL volume (or saturation reduction) and changes in LNAPL composition on dissolved plume concentration are illustrated in Figure 5. In this conceptualisation, the LNAPL source material A changes composition to C, which has a reduced concentration of benzene. Thus, the dissolved benzene concentration in groundwater is also reduced. However, when only the LNAPL volume or pore saturation of LNAPL A is reduced to B without any compositional change, this has little effect on the benzene concentrations in groundwater.

This concept is apparent in large-scale studies of dissolved petroleum hydrocarbon attenuation at LNAPL sites (Kamath *et al* 2011; Mace *et al* 1997; Newell & Connor 1998; Rice *et al* 1995). These studies observed that dissolved constituent attenuation rates were comparable at sites where conventional active LNAPL remedial techniques were implemented to those where no active remediation was implemented. Accordingly, the studies concluded that natural attenuation was the dominant dissolved plume attenuation mechanism whether or not conventional active LNAPL source remediation attempts were made. Similarly, dissolved phase petroleum hydrocarbon plumes have been demonstrated to be largely stable in extent for finite releases. For example, Kamath *et al* (2011) examined data for 48 sites and found 95% of benzene plumes were stable or shrinking. Connor *et al* (2015) published a survey of studies encompassing thousands of sites and found 94% of dissolved benzene plumes were stable (non-increasing concentration trends).

Dissolved phase stability is often pointed to as an indicator of the stability of the LNAPL body source material (CL:AIRE 2014; CRC CARE 2015; ITRC 2018). The existence of a large body of work indicating dissolved petroleum hydrocarbon plumes are overwhelmingly found to be stable therefore supports the earlier discussion regarding the typical stability of LNAPL body source zones.

It is also well-established that petroleum vapours readily biodegrade over short distances in the vadose zone and contemporary petroleum vapour intrusion (PVI) screening distances based on empirical data have reduced considerably compared with historical guidance based on models that did not adequately account for biodegradation. The mechanics of PVI, the appropriate application of screening distances, monitoring methodologies, and considerations with respect to PVI in LNAPL site management are detailed in existing guidance from CRC CARE (2013), the United States Environmental Protection Agency (US EPA 2015) and ITRC (201).

KEY POINTS:

1. **Concentrations of constituents in the dissolved and vapour phases are relatively insensitive to LNAPL volume or saturation levels.**
2. **Changes in LNAPL volume or saturation levels that do not alter LNAPL composition will not result in a commensurate change in dissolved or vapour phase constituent concentrations.**
3. **Significant reductions in LNAPL volume/saturation may result in some reduction in dissolved or vapour plume longevity.**
4. **Most dissolved phase plumes will be found to be stable.**
5. **Natural attenuation will typically achieve most of the dissolved plume attenuation with or without conventional active LNAPL recovery/source reduction attempts.**

2.3 Long-term LNAPL body evolution

Over time, changes in an LNAPL body will serve to further enhance stability and progressively diminish the fraction of the LNAPL body that is potentially hydraulically mobile/recoverable. In addition, the potential for constituents within the LNAPL to dissolve and volatilise will diminish over time due to compositional changes. These changes will largely be controlled by hydraulic conditions and are influenced by NSZD processes.

The term smearing refers to the vertical redistribution of LNAPL caused by natural/seasonal fluctuations in hydraulic conditions (i.e. water table elevation) that progressively reduces the fraction of the LNAPL body that might be mobile/recoverable over time. Frames 10–12 in Figure 1 are a conceptualisation of the effects that smearing has on an unconfined LNAPL body in a soil/aquifer setting. If water table fluctuations are sufficiently large and enough mobile LNAPL is present, smearing can increase the overall LNAPL extent (vertically). At the same time, localised saturation levels are reduced by the spreading of the fixed volume of LNAPL over a larger depth interval. Each time the water table rises or falls, a portion of the mobile fraction of the LNAPL will move with the water table and a portion will remain trapped in the pore space, such that the mobile fraction that persists is smaller each time (ITRC 2018). In a fractured rock setting, water table fluctuations can have the effect of increasing the period of time where LNAPL expansion can occur compared with LNAPL in soil (Hardisty 2010). Therefore, water table fluctuations have different effects on an LNAPL body depending on the setting:

- Soil – water table fluctuations will provide an additional stabilising effect on an LNAPL body through the progressive immobilisation of the LNAPL via smearing.
- Fractured rock – water table fluctuations can increase the overall LNAPL extent and time to LNAPL body stabilisation compared with LNAPL in soil. It is noted that the opposite can also occur in that fracture networks that are not highly interconnected can significantly limit LNAPL footprint for a given release scenario compared with LNAPL in soil.

Changes in hydraulic conditions therefore play a role in the progressive immobilisation of LNAPL over time. This enhances the overall stability of the LNAPL body and decreases how much of the LNAPL might be recoverable. This effect can be significant. Most LNAPL bodies that have been in the subsurface for timeframes on the order of years will be found to exist at relatively low LNAPL saturation levels that will predominantly comprise hydraulically immobile and unrecoverable residual LNAPL (ITRC 2018). API (2018) indicates that LNAPL saturations at this stage will typically be found in a very low range of 1–10%. Contrasting this with residual thresholds that are commonly as high as 30% in porous media (CRC CARE 2015) provides an indication that typical LNAPL saturation levels will be within a range that would be considered effectively immobile and unrecoverable.

To further illustrate, Figure 6 presents results of soil core petrophysical testing where LNAPL saturations were quantified before and after bench-scale LNAPL mobility testing. It plots the initial (pre-test) LNAPL saturations against the final (post-test) LNAPL saturations in order to assess what portion of the sample group exhibited large recoverable fractions (i.e. where a significant reduction in LNAPL saturation was observed during testing). Where no LNAPL was released, the final or post-test LNAPL saturations can be assumed to be in the residual range. This plot shows that greater than 85% of tested locations across twenty randomly selected sites exhibited residual level (i.e. unrecoverable) LNAPL saturations that were as high as 35%.

While the typical case is described above, there are exceptions and clearly some LNAPL sites will contain more highly LNAPL-saturated areas (i.e. well above residual saturation levels) and, therefore, potentially large recoverable fractions. As previously discussed, LNAPL will be at its most mobile and potentially recoverable during and shortly after a release and this will progressively decrease over time. Accordingly, the closer in time a site is to the release, the more potentially relevant the consideration of LNAPL recovery will be and the greater potential benefit it will have. Similarly, the potential relevance and benefit of LNAPL recovery will usually decrease over time as the LNAPL body stabilises and the recoverable fraction diminishes. The question of when LNAPL mass recovery efforts may be technically needed and/or might provide a beneficial change in conditions remains a prominent consideration in LNAPL site management, and the answer to this question will be highly site-specific and will almost always require a multiple lines of evidence approach. Table 1 provides potential metrics that can be applied when determining the degree of LNAPL mobility and, therefore, the practicability and/or potential benefit of LNAPL recovery.

Other drivers such as regulatory requirements may require LNAPL recovery in the absence of technical need/benefit. In these cases, the metrics in Table 1 may still be applied in order to set realistic expectations as to what might be accomplished with the implementation of such an activity. It is also noted that in-well LNAPL thickness is not listed in Table 1. In general, the magnitude of in-well LNAPL thickness is now widely recognised to be a poor/unreliable metric when assessing LNAPL mobility and recoverability for the following reasons (API 2018; ASTM 2014; CL:AIRE 2014; CRC CARE 2015; Hawthorne *et al* 2015; ITRC 2018):

- Low recoverability can be associated with very large in-well thicknesses and small in-well thicknesses can sometimes be associated with high recoverability.
- Large in-well thicknesses can be observed within LNAPL bodies that are stable and largely present at residual levels.

- Large in-well thicknesses can persist at sites even after aggressive LNAPL recovery systems have been applied to a practical endpoint.

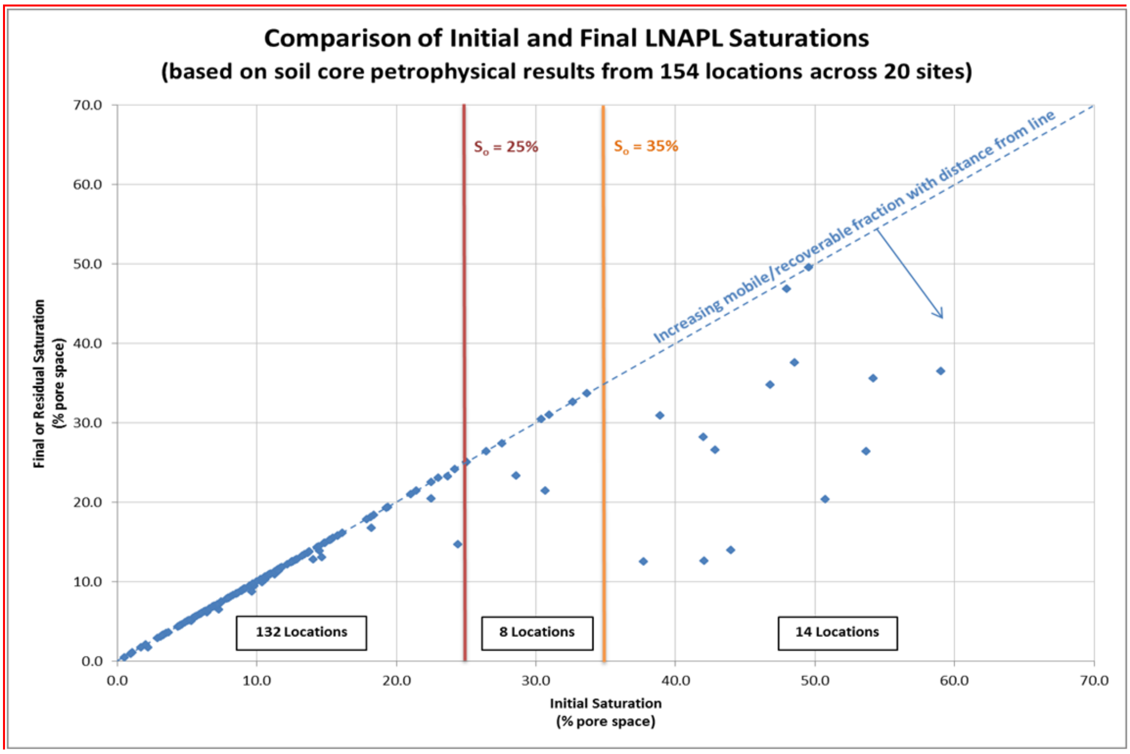

Figure 6: Results of LNAPL mobility testing on soil core samples from twenty randomly selected sites with varied LNAPL types and settings. Data points on the diagonal line indicate samples where LNAPL saturations were at residual levels and a significant recoverable fraction was not observed. Note: S_o = oil/LNAPL saturation (Rousseau 2015).

Further discussion of the interpretation of in-well LNAPL thickness data is provided in Appendix A. Additional lines of evidence relating to LNAPL mobility, recoverability and overall stability are provided in Appendix C. ITRC (2018) presents a comprehensive discussion detailing why T_n represents a better metric for recoverability than in-well LNAPL thickness and the empirical basis for the suggested *de minimis* LNAPL transmissivity/recoverability range of 0.01–0.08 m^2/day (0.1–0.8 ft^2/day).

KEY POINTS:

1. **Water table fluctuations can both limit and exaggerate LNAPL body extent depending on stratigraphy and hydrogeologic conditions.**
2. **Smearing progressively immobilises LNAPL, thereby enhancing LNAPL body stability and reducing the fraction of the LNAPL body that is potentially recoverable over time.**
3. **Older LNAPL bodies will largely be present at low/residual saturation levels.**

Table 1: Potential threshold metrics and criteria that can be applied when determining the practicability and/or potential benefit of LNAPL mass recovery

Threshold metric	Associated criteria	Notes
LNAPL transmissivity (T_n)	T_n demonstrated to significantly exceed 0.01–0.08 m^2/day (0.1–0.8 ft^2/day)[a] *de minimis* range across a large portion of an LNAPL body	• Widely adopted as a primary metric for technical feasibility and potential benefit of LNAPL recovery • Where T_n is *de minimis*, it can be assumed that most of the LNAPL is residual and LNAPL mass recovery efforts will not provide a technical benefit (ITRC 2018) • Where T_n indicates LNAPL recovery is technically feasible at one or more locations, consider the distribution of T_n across the LNAPL body extent and the potentially recoverable fraction to assess the potential overall benefit of the activity
LNAPL saturation	LNAPL saturations are demonstrated to be well above residual levels across a significant portion of an LNAPL body	• Indicates a significant recoverable fraction • Saturations and residual saturations can be determined directly or through the conversion of total petroleum hydrocarbon concentrations to saturations and comparison against literature values for residual levels[c]
LNAPL recovery system performance	Decline curve[b] indicates more than 10% of the potentially recoverable LNAPL remains	• Indicates a significant recoverable fraction remains
	System performance exceeds one-half of NSZD rates	• Indicates an incremental benefit in system operation over NSZD alone

[a] *de minimis* LNAPL recoverability range recommended by ITRC (2018). Also, certain jurisdictions in the USA have adopted 0.05 m^2/day (0.5 ft^2/day) as a *de minimis* criterion (e.g. States of Michigan, Nebraska, Massachusetts).
[b] see Appendix D for example decline curve analysis.
[c]Adamski *et al* (2003), API (2004) and ASTM (2014) provide information on converting TPH concentrations to saturations and typical residual levels for different soil types. Literature values for saturated zone residual saturations vary from 5–30% depending on soil type, with coarser soils able to hold more LNAPL and therefore have larger residual levels. The empirical data in Figure 6 indicates that larger recoverable fractions were consistently noted at LNAPL saturation levels exceeding 25–35% across a range of LNAPL types and soil settings.

2.4 Natural source zone depletion (NSZD)

NSZD refers to the combined effects of dissolution of LNAPL constituents and saturated zone biodegradation, volatilisation of LNAPL constituents and vadose zone biodegradation, as well as biodegradation of the LNAPL body itself. A conceptual depiction of these processes is shown in Figure 7. Until recently, guidance on natural attenuation at LNAPL sites has focused on the dissolved phase and the applicability of monitored natural attenuation (MNA) as a sustainable groundwater remedial approach at low risk sites. However, it is now understood that evidence of NSZD can be mostly observed in the vadose zone and can exceed dissolved phase attenuation rates by orders of magnitude (API 2017; CRC CARE 2018, ITRC 2018;Lundegard & Johnson 2006; Molins *et al* 2010).

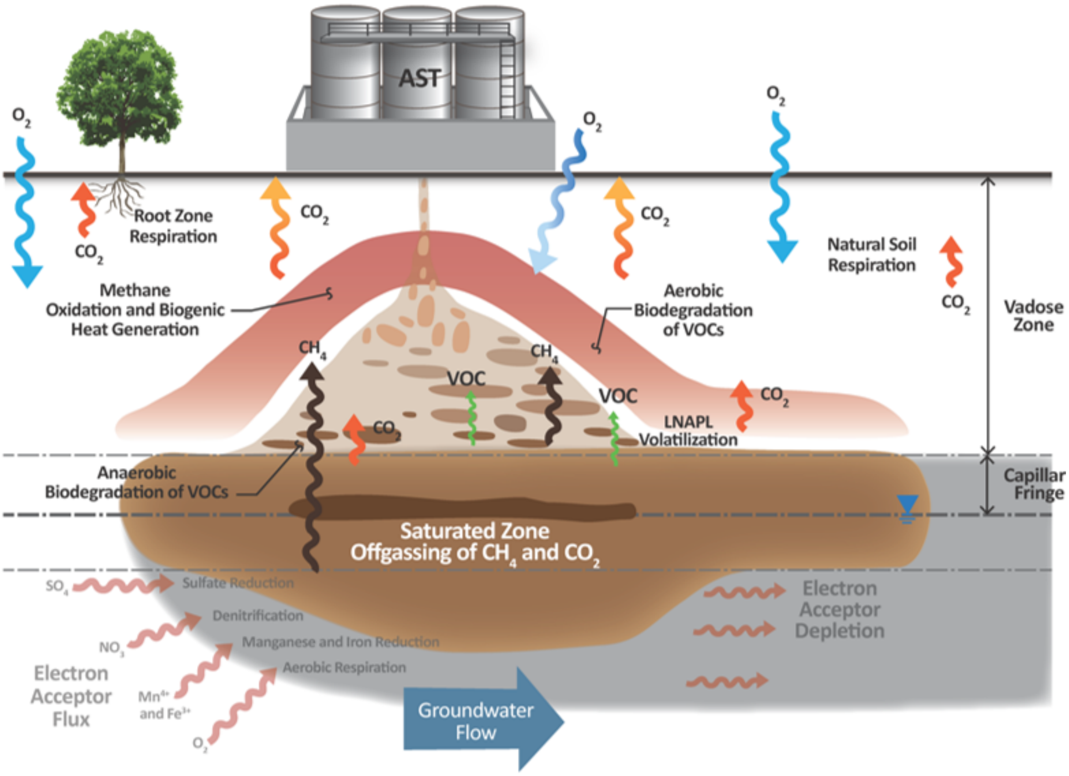

Figure 7: Conceptualisation of LNAPL NSZD processes (from API 2017)

As shown in Figure 7, the degradation of LNAPL will generally proceed anaerobically via methanogenesis, producing methane (CH_4) and carbon dioxide (CO_2), with CH_4 subsequently oxidised to CO_2 exothermically in the vadose zone. Aerobic biodegradation of LNAPL vapours in the subsurface may periodically dominate methanogenesis as a mass loss mechanism for NSZD (Sookhak Lari *et al* 2019). Either NSZD process produces changes in the concentrations of certain vadose zone gases (CH_4, CO_2, O_2, and volatile constituents/volatile organic compounds (VOCs)) and increases in temperature that may be measurable. The rate of degradation is temperature dependent and can occur more rapidly in warmer climates.

A simplified one-dimensional conceptual model showing NSZD processes in the saturated and unsaturated zones, along with the possible fluxes of these gases is provided in Figure 8 for the methanogenesis-dominated case. Accordingly, the most common ways by which NSZD is confirmed and quantified focus on:

1. concentration changes of CO_2, O_2, CH_4 and VOCs in the vadose zone
2. near surface CO_2 flux out of the ground (efflux), and/or
3. temperature gradients in the vadose zone.

In addition, LNAPL natural losses may be quantified through observed changes in LNAPL composition over time. CRC CARE Technical Report 44 details a range of methods, including guidance on best practices for implementation.

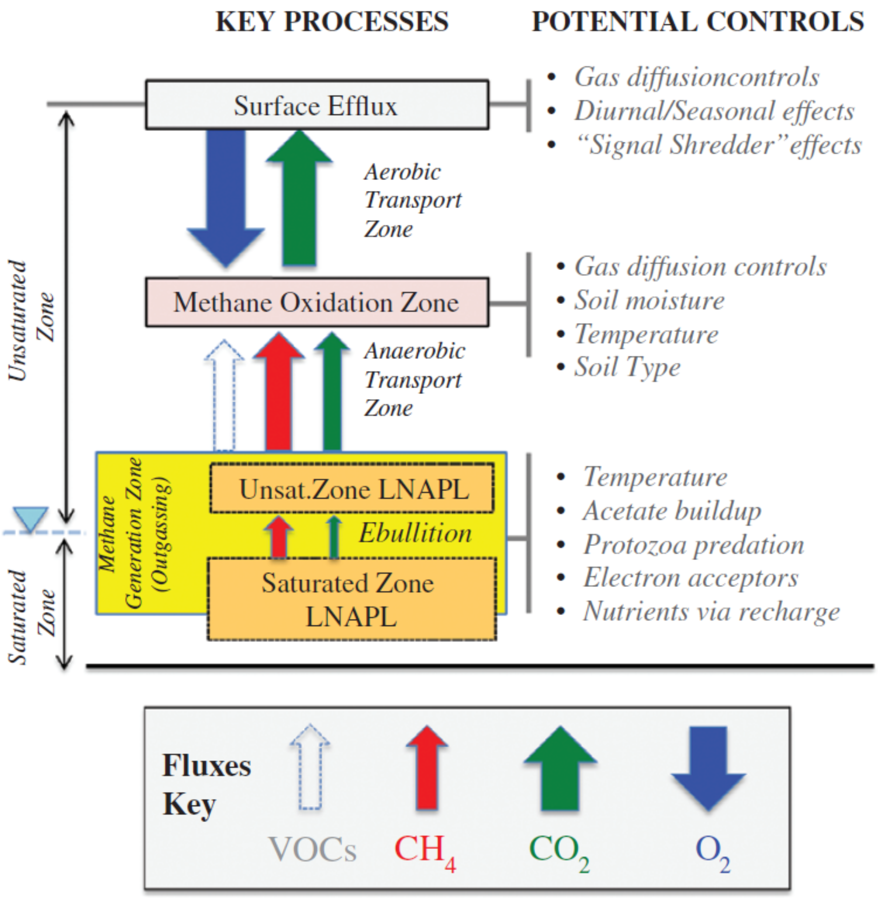

Figure 8: One-dimensional conceptual model of NSZD processes and gas flux (Garg *et al* 2017)

NSZD processes occur to some degree at all LNAPL sites (CL:AIRE 2019). Typical LNAPL mass depletion rates are of sufficient magnitude to indicate that the capacity for LNAPL to be degraded in the subsurface has been greatly underestimated historically (Suthersan et al 2015). Garg *et al* (2017) and Sookhak Lari *et al* (2019) provide reviews of NSZD processes and a summary of research from similar processes involving other methanogenic systems (e.g. anaerobic digesters, landfills) showing that the relative magnitudes of NSZD rates reported in the literature were realistic in comparison (Table 2).

Table 2: Representative degradation rates from different systems (Garg *et al* 2017)

System type	Representative equivalent LNAPL degradation rate (L ha^{-1} yr^{-1})
Anaerobic digesters	5,000,000
Ethanol release sites	200,000
Landfills	100,000
LNAPL NSZD	**20,000**
Wetlands	2,000
Peat	40

This represents a paradigm shift from an electron acceptor-based dissolved phase model of natural hydrocarbon attenuation to one based on methanogenesis with gas transport through the vadose zone as the primary mass loss mechanism (Garg *et al* 2017). This shift is illustrated in Table 3.

As noted in Tables 3 and 4, it is common to find NSZD rates at LNAPL sites on the order of 1,000s to 10,000s litres of LNAPL depleted per hectare per year (100s to 1,000s of U.S. gallons of LNAPL depleted per acre per year in the units common to most of the available NSZD literature). Table 4 shows that NSZD rates measured in Australia are comparable to, or greater than, what is considered typical overseas, which may be attributable to higher average ambient and subsurface temperatures in Australia since NSZD rates will be temperature dependent. As such, the incorporation of NSZD as a component in the management of LNAPL sites has been demonstrated to be viable. Table 4 also shows the scale of LNAPL NSZD observed in vadose zones (NSZD) compared to within groundwater (MNA). As shown here, the dissolved phase degradation rates are at least an order of magnitude lower than what has been quantified through vadose zone monitoring, which supports the conceptualisation of NSZD described above.

Table 3: Paradigm shift from MNA to NSZD (adapted from Garg *et al* 2017)

Item	Hydrocarbon attenuation in the 1990s–2000s	Hydrocarbon attenuation now
Nomenclature	Monitored natural attenuation (MNA) of dissolved plume	Natural source zone depletion (NSZD) of LNAPL body
Management focus	Plume length	Source longevity
Key constituents	Dissolved BTEX	All LNAPL constituents
Key biodegradation process	Electron acceptor mediated biodegradation	Methanogenesis
Key unsaturated zone biodegradation process	Volatilisation of LNAPL followed by aerobic biodegradation of hydrocarbon vapours	Anaerobic biodegradation (methanogenesis) of LNAPL followed by aerobic methane oxidation
Key saturated zone biodegradation process	Anaerobic biodegradation of dissolved BTEX	Anaerobic biodegradation of LNAPL by methanogenesis with off-gassing and ebullition
Key metric	Biodegradation capacity	NSZD rate
Key measurement	Upgradient vs. downgradient electron acceptors and byproducts	CO_2 efflux, gradient of O_2 consumption in vadose zone, thermal flux, compositional change
Representative attenuation rates	BTEX half-life of 2–4 years	NSZD rates of 1,000s to 10,000s L LNAPL ha^{-1} yr^{-1}

Table 4: Comparison of NSZD rates reported in the literature with Australian results

Location	Measurement type	Number of sites	Estimated rates (L LNAPL ha^{-1} yr^{-1})	Source
North America	NSZD (vadose)	25	3,000–80,000	Garg *et al* 2017
	MNA (dissolved)	9	4–500	
Australia	NSZD (vadose)	5	0–87,000[a,b]	Rayner *et al* 2020
Australia	NSZD (vadose)	8	10,000–220,000[a,b]	GHD

[a] range of maximum rates across respective sites

[b] a more detailed summary for a sample group of these sites is provided as case studies in Section 4 and Appendix E

As previously discussed, LNAPL bodies are largely self-stabilising in relatively short timeframes following the cessation of a release. However, small LNAPL gradients/fluxes are commonly observed to persist at LNAPL sites. Mahler et al (2012) showed that natural LNAPL losses (i.e. NSZD) can balance these small fluxes, and this can be a key mechanism in maintaining long-term LNAPL stability. Therefore, similar to the well understood concept that dissolved phase natural attenuation processes are key in degrading and limiting the extents of dissolved petroleum hydrocarbon plumes, NSZD processes appear to be key in both the degradation and stabilisation of the LNAPL body source material.

NSZD processes may therefore have a significant effect on the behaviour and life of LNAPL in the subsurface. Accordingly, there are a number of possibilities for how NSZD can be a component of an LNAPL management strategy:

- **During LCSM development** as a baseline evaluation of LNAPL degradation, and to better understand and support conclusions regarding LNAPL stability.
- **During remedial options assessment** as a component of a remedial/management strategy, and to better understand the benefits of active LNAPL recovery compared with the benefits of NSZD.
- **During remediation/management** as a primary LNAPL management technique, as a secondary approach following active recovery methods, and/or as a consideration when assessing whether an acceptable endpoint to active remediation has been reached. Since NSZD is a ubiquitous naturally occurring phenomenon, it will be part of all LNAPL site management strategies by default. As a standalone remedy, NSZD will be most applicable where LNAPL is stable, LNAPL recovery is technically impracticable and/or will not provide a benefit, and there are no unacceptable human health or environmental exposures (or exposures can be effectively mitigated with controls).

The incorporation of NSZD at different points in an overall LNAPL site management strategy is detailed further in Section 3.

KEY POINTS:

1. **NSZD is a ubiquitous naturally occurring phenomenon that will therefore be part of all LNAPL management strategies by default.**
2. **NSZD both reduces LNAPL mass/saturation and changes LNAPL composition over time.**
3. **NSZD is a factor in long-term LNAPL body stability.**
4. **NSZD rates observed in Australia are comparable to or exceed what is considered typical overseas.**
5. **NSZD will be most appropriate as a standalone remedy where LNAPL is stable, recoverability is *de minimis*, and exposures are mitigated or controlled.**

2.5 Summary

The preceding discussion presented some of the key LNAPL fundamentals that can impact the development of LCSMs and site management strategies, particularly in the consideration of the potential role of NSZD. A summary of the key points is provided below that are integrated into the site management process in Section 3.

- **LNAPL body formation and dynamics:** LNAPL bodies consist of continuously variable proportions of LNAPL, water and/or air coexisting in the pore space both above and below the water table (think iceberg, not pancake). The pore space at LNAPL sites will therefore never be completely filled with LNAPL. Typically, LNAPL bodies stabilise on a timescale that can vary from days to years depending on the volume of the release, the LNAPL type, and subsurface conditions.
- **Constituent partitioning:** Concentrations of constituents in the dissolved and vapour phases are relatively insensitive to LNAPL volume or saturation levels. Therefore, changes in LNAPL volume or saturation levels that do not alter LNAPL composition will not result in a commensurate change in dissolved or vapour phase constituent concentrations. However, a reduction in the extent of the dissolved plume can result where significant reductions in LNAPL volume/ saturation are considered to be feasible/warranted. Most dissolved phase plumes will be found to be stable, with natural attenuation generally responsible for most of the dissolved plume attenuation observed at LNAPL sites. This has been shown to predominantly be the case with or without conventional active LNAPL recovery/source reduction attempts.
- **Long-term changes in hydraulic conditions:** Water table fluctuations can both limit and exaggerate LNAPL body extent depending on site conditions. Smearing progressively immobilises LNAPL, thereby enhancing LNAPL body stability and reducing the fraction of the LNAPL body that is potentially recoverable over time, with older LNAPL bodies largely found to be present at low/residual saturation levels. LNAPL will be at its most mobile and potentially recoverable during and shortly after a release and this will progressively decrease over time. Consequently, the closer in time a site is to the release, the more potentially relevant the consideration of LNAPL recovery will be and the greater potential benefit it will have. Similarly, the potential relevance and benefit of LNAPL recovery will decrease over time as the LNAPL body stabilises and the recoverable fraction diminishes. The evaluation of LNAPL mobility and potential recoverability

is a very site-specific endeavour that can be supported by science-based metrics such as LNAPL transmissivity.

- **Natural source zone depletion:** NSZD is a ubiquitous naturally occurring phenomenon that will therefore be part of all LNAPL management strategies by default. Because NSZD depletes LNAPL mass through biodegradation, it has the combined effect of reducing LNAPL saturation and changing LNAPL composition over time. NSZD processes have also been shown to play a role in the long-term stability of LNAPL bodies by balancing the typical fluxes that occur in mature/stable LNAPL bodies. Work by CSIRO and other practitioners has shown that NSZD rates observed in Australia are comparable to or exceed what is considered typical overseas. NSZD is therefore a viable consideration in LNAPL site management in Australia with a number of possibilities for how NSZD can be a component of an LNAPL management strategy including during LCSM development, during remedial options assessment, and as part of the ultimate remediation/management strategy. As a standalone remedy, NSZD will be most applicable where LNAPL is stable, LNAPL recovery is technically infeasible and/or will not provide a benefit, and there are no potential exposures (or exposures can be effectively mitigated with controls).

3. LNAPL site management strategy

LNAPL site management strategy has evolved considerably in the last ten years, as evidenced by the significant number of new documents published on the subject in Australia (e.g. CRC CARE 2015) and overseas (e.g. ASTM 2014; CL:AIRE 2014; ITRC 2009; ITRC 2018). The overarching theme is a movement toward a more science- and risk-based approach to LNAPL remediation and management that is similar to how contamination in other phases (soil, groundwater, soil gas) has been viewed and addressed for some time. Some of the main shifts in LNAPL management approaches documented in the more recent guidance include:

- Movement away from an assumed correlation between magnitudes of in-well LNAPL thickness and LNAPL mobility potential or recoverability.
- Replacement of in-well LNAPL thickness as a primary LNAPL mass recovery threshold and end-point metric with more science-based metrics such as LNAPL transmissivity.
- More focus on controls as potentially more implementable and effective for risk mitigation than source removal due to the impracticability of LNAPL mass recovery that will be experienced at many LNAPL sites.
- Acknowledgement of significant role of bioattenuation of petroleum vapour leading to much smaller separation distances between source and receptor being considered protective compared with what was typical historically.
- Increased interest in sustainable remediation and concepts such as the net environmental benefit of active/engineered approaches.

The most recent guidance documents from CRC CARE (2018), ITRC (2018), API (2018) and CL:AIRE (2019) have additionally started to address how NSZD is monitored and/or how it can fit into LNAPL site management strategy. In this section, the current understanding of LNAPL fundamentals discussed in Section 2 will be woven into an overall process that will support sound technical decision-making in LNAPL site management while considering the role of NSZD.

As noted in CRC CARE Technical Report 34, a sense of proportionality should be maintained in the use of this guide and in the management of LNAPL. Site sensitivity, intergenerational equity and the economics of remediation are key considerations in the decision-making process. The derivation of stakeholder-endorsed remedial objectives and the acceptance of LNAPL remediation end points rely heavily on the quality of the LCSM and the professional judgement of remediation practitioners. Each of these considerations is contemplated further in the remainder of this section.

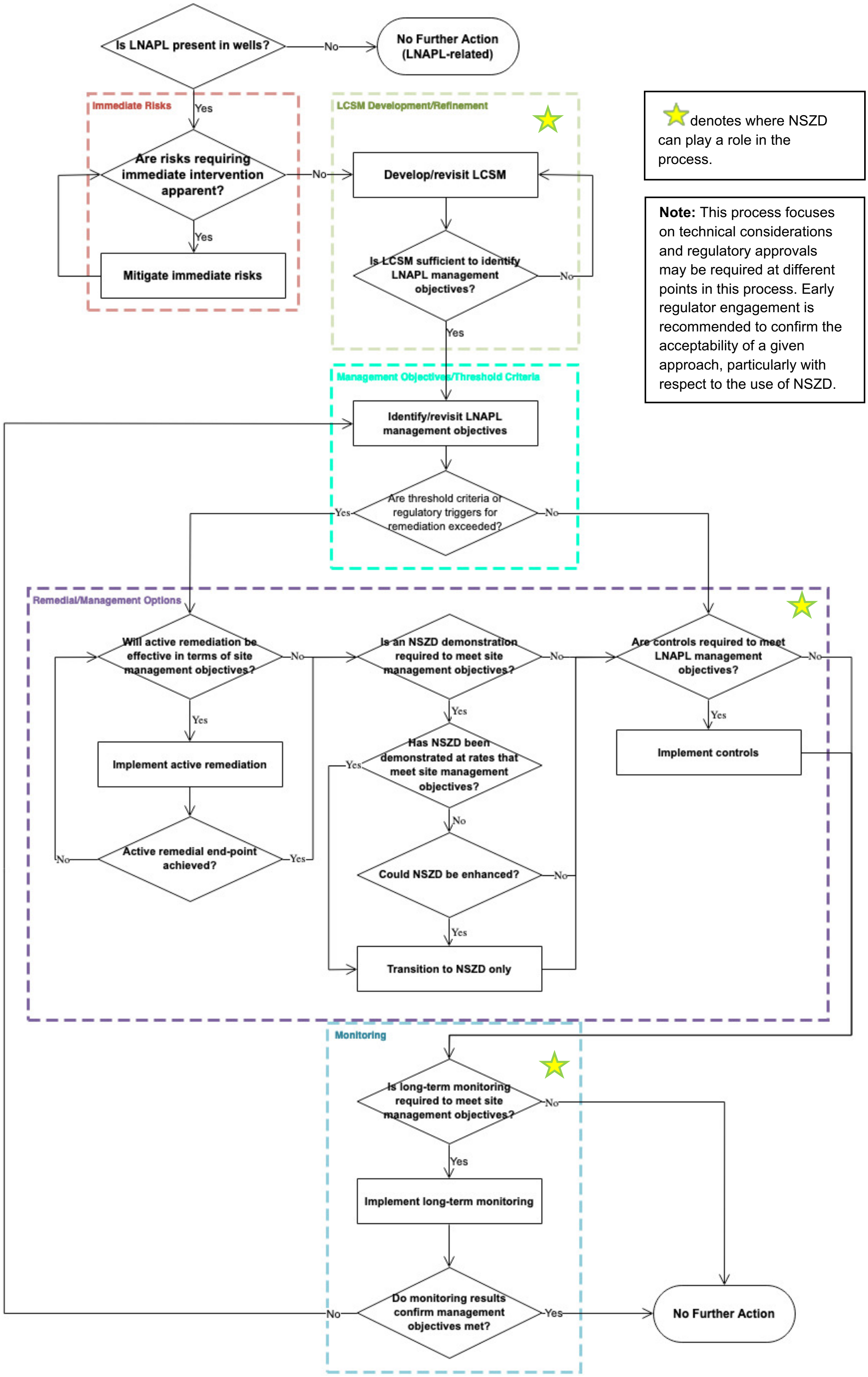

Figure 9: LNAPL site management decision-making framework

Figure 9 proposes an LNAPL site management decision-making framework with the goal of maximising the effectiveness and net environmental benefit of an LNAPL site management strategy by considering potential science-based remedial objectives and threshold metrics, regulatory requirements, and the role of NSZD. The remainder of this section is organised to follow the flow of the framework in order to provide a logical progression of supporting documentation and considerations at each stage.

3.1 LNAPL presence

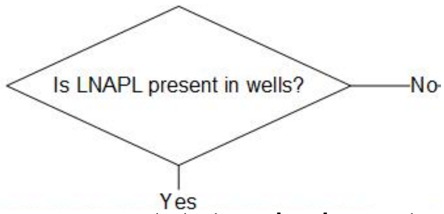

Figure 10: Initial trigger for LNAPL management strategy development

The presence of LNAPL in wells is a typical trigger for the commencement of LNAPL site management and potentially for regulatory agency notification depending on jurisdiction. As discussed in Section 2, the presence of LNAPL in wells indicates that some LNAPL exists at saturation levels above residual. However, LNAPL that is not present at high enough saturation levels (above residual) will not be able to flow into a well. It is important to note that while the presence or absence of LNAPL in wells is typically interpreted as a significant difference in terms of level of concern, there may actually be only small differences in LNAPL saturation levels between these two conditions in the formation.[4] Monitoring wells that are not constructed appropriately can also prevent mobile LNAPL from entering even though it is present in the adjacent subsurface (e.g. water table consistently above the top of screen in an unconfined setting).

Because most older LNAPL bodies are expected to largely exist at residual saturation levels, most older LNAPL bodies will contain a significant volume fraction that will not be observable in wells. It is therefore typical to use other methods in addition to monitoring well observations to infer/define the extent of an LNAPL body. Potential options in this regard are presented in Appendix B.

[4] *More information on interpreting in-well LNAPL thickness data is provided in Appendix A.*

3.2 Immediate risks

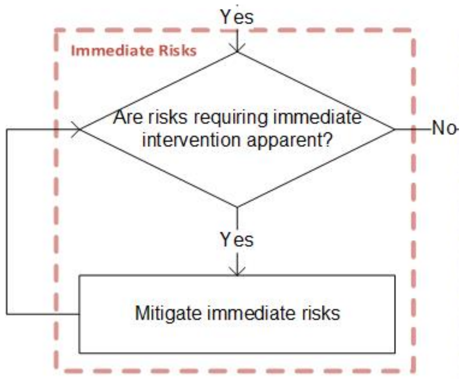

Figure 11: Consideration of immediate risks in the LNAPL management strategy

Immediate risks might be LNAPL migration offsite or close to sensitive receptors (e.g. buildings, bodies of water), an LNAPL release being very close to ground surface or at ground surface posing acute exposure (e.g. dermal contact or vapour inhalation) or potential explosion hazards. Also, if groundwater plumes might be migrating substantially offsite or impacting receptors or water supplies. Other types of acute exposure hazards may exist that require a remedial response or controls to be implemented, particularly where a volatile LNAPL type such as petrol is present. For example, risks to human health and potentially explosive environments resulting from vapour intrusion into structures (e.g. petroleum vapours or methane above action levels). In addition, appropriate protocols pertaining to health and safety when working with and around flammable and/or combustible liquids may be applicable depending on the nature of site works.[5] In the absence of any of the aforementioned immediate or acute risks, the LNAPL management strategy can progress to a more typical LCSM development phase in order to gain a better understanding of site conditions and potential drivers that will form the basis of the longer-term LNAPL management strategy.

3.3 LCSM development

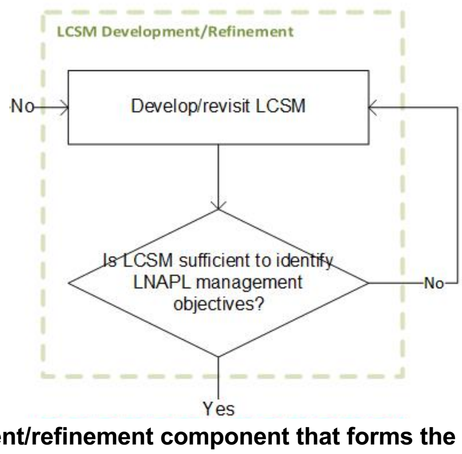

Figure 12: LCSM development/refinement component that forms the basis for establishing site management objectives

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[5] *For more information, consult the National Code of Practice for the Storage and Handling of Dangerous Goods [NOHSC: 2017(2001)]*

Comprehensive LCSM development is key to effectively understanding site conditions and to establish site management objectives and inform site management decision-making. The LCSM should be viewed as scalable based on the complexity of the site and potential risks. In addition, LCSM development/refinement will typically be an iterative process that will be revisited whenever new information becomes available for a given site. Views on site management objectives and, therefore, the site management strategy that flows from those objectives, may therefore evolve over time. Tools and considerations for LCSM development have been previously presented in CRC CARE Technical Report 34. More recently, ITRC (2018) provides the most comprehensive/detailed procedure and toolbox for LCSM development to date. The reader is encouraged to consult these publications for more information. On a fundamental level, the LCSM will need to consider where the LNAPL is, how it is moving, how recoverable it may be, what potential exposures may exist, and what the role of NSZD is at a minimum. Typical items to consider will include:

- LNAPL release details
- LNAPL type/composition
- LNAPL body distribution and extent
- LNAPL mobility, recoverability and overall stability
- site geology/hydrogeology
- dissolved and vapour plumes
- site setting/land use
- potential receptors and exposure pathways, and
- natural attenuation (NSZD, MNA).

A list of key questions to guide LCSM development related to the items listed above is provided in Figure 13 by expanding the LCSM development component of the decision tree (Figure 9). The available site data at any point during LCSM development and professional judgement will dictate the prioritisation of these questions and the extent to which different lines of evidence are developed to answer them. For example, small sites with LNAPL and dissolved phase plumes that are stable, completely onsite, and unlikely to impact receptors may not require the use of sophisticated tools or extensive LCSM development to adequately inform the remainder of the site management process. On the other hand, large and/or complex sites with offsite impacts are more likely to require the use of sophisticated tools/approaches and larger data sets developed over longer time periods in order to fully understand and adequately develop the LCSM.

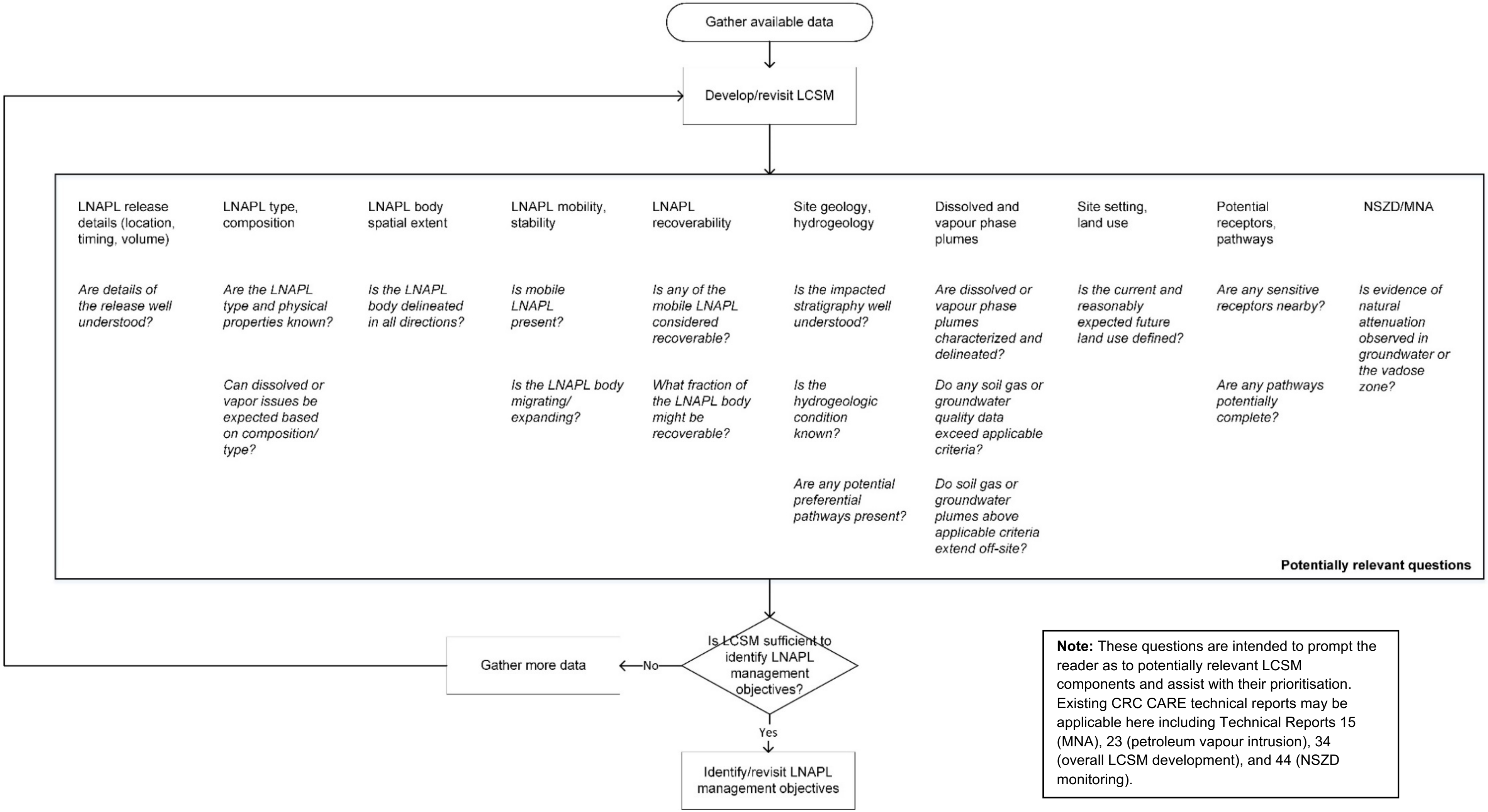

Figure 13: Expanded LCSM development/refinement component

As previously mentioned, other key considerations in LCSM development include how the LNAPL body is moving and how much of it might be recoverable. The evaluation of the mobility, recoverability and overall stability of the LNAPL body is often not straightforward and will also require a multiple lines of evidence approach. Appendix C provides options for different lines of evidence that may be examined in this regard.

Clearly, the evaluation of potential exposures that may be present at any point will be particularly important in LCSM development and the identification of LNAPL site management objectives discussed in the next section. This will most often involve the comparison of site analytical results against generic risk-based regulatory criteria, which may then progress to quantitative Health and Ecological Risk Assessment (HERA) to evaluate site-specific acceptable exposure levels depending on site complexity and risk profile. This aspect of LCSM development has been thoroughly addressed in existing regulatory guidance (both state-specific guidance and the National Environment Protection Measure (NEPM) and by CRC CARE (e.g. CRC CARE Technical Reports 10, 34) and will not be repeated here.

The presence of LNAPL does not necessarily indicate that there is an unacceptable risk; instead, the level of risk should be determined through a careful process of risk assessment. Things to keep in mind when assessing potential LNAPL site risks are:

- LNAPL is typically self-stabilising over relatively short timeframes; therefore, the risk of new LNAPL body migration or expansion is relatively short-lived.
- Dissolved plumes should be expected to be stable typically (with the exception of recent releases).
- Dissolved plumes at LNAPL sites are often reported from groundwater sample locations where LNAPL/sheen was present in the well or in the vicinity. It is a common problem that LNAPL will contaminate groundwater samples and bias results high such that they are not representative of groundwater quality. This can imply exposure concerns that may not actually exist. The potential contamination of groundwater samples by LNAPL can be assessed by comparing analytical results for a given constituent to its effective solubility. Effective solubilities can be calculated based on a constituent's solubility and its mole fraction in the parent LNAPL where LNAPL composition is known.[6] In addition, API (2004) offers reference tables of typical values for constituents of common LNAPL types.
- Petroleum vapours readily biodegrade in the subsurface over short distances (see CRC CARE Technical Reports 12 and 23).

[6] *Also see U.S. EPA's effective solubility calculator at https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/es.html*

3.4 Identification of LNAPL site management objectives

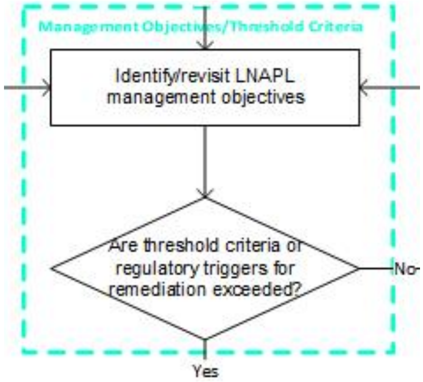

Figure 14: Establishment of LNAPL management objectives and consideration of remedial threshold metrics and regulatory requirements to guide the LNAPL management strategy

The development of a comprehensive LCSM facilitates the assessment of potential LNAPL management objectives. ITRC (2018) categorises management objectives as either saturation-based or compositional. Saturation-based objectives principally pertain to the stabilisation of an LNAPL body, whereas compositional objectives relate to the mitigation of exposures resulting from LNAPL composition (i.e. largely dissolved phase or vapour concerns). Most simply, potential LNAPL site management objectives (both regulatory and technical) will broadly fit into one or more of the options listed in Table 5. Each objective will also be associated with certain threshold criteria and more specific goals that will dictate the overall management strategy. More specific metrics that define practicable limits that may be applied as both remedial threshold and success/end-point criteria are provided in Table 8.

Table 5: Possible LNAPL site management objectives, threshold criteria and applicable goals

Objective	Threshold criteria	Applicable goals
Saturation-based		
Mitigate LNAPL body migration potential (stabilise LNAPL body)	Multiple lines of evidence indicate LNAPL body migration or expansion (see Appendix C)	1. Remove enough LNAPL to abate migration potential 2. Recover LNAPL to a practicable limit, and/or 3. Mitigate migration potential through controls.
Recover LNAPL to an arbitrary endpoint*	LNAPL thickness in wells	1. Recover LNAPL until an arbitrary in-well thickness target is met
Compositional		
Mitigate unacceptable health or ecological exposures	Exceedance of generic regulatory criteria coupled with a potentially complete pathway Results of quantitative HERA indicates unacceptable exposure potential	8. Remove enough LNAPL to mitigate exposure potential 9. Mitigate exposure potential through LNAPL compositional change/degradation, and/or 10. Mitigate exposure potential though controls.

*Driven by regulatory requirements or non-technical objectives where there is no technical driver

3.5 Remedial/management options

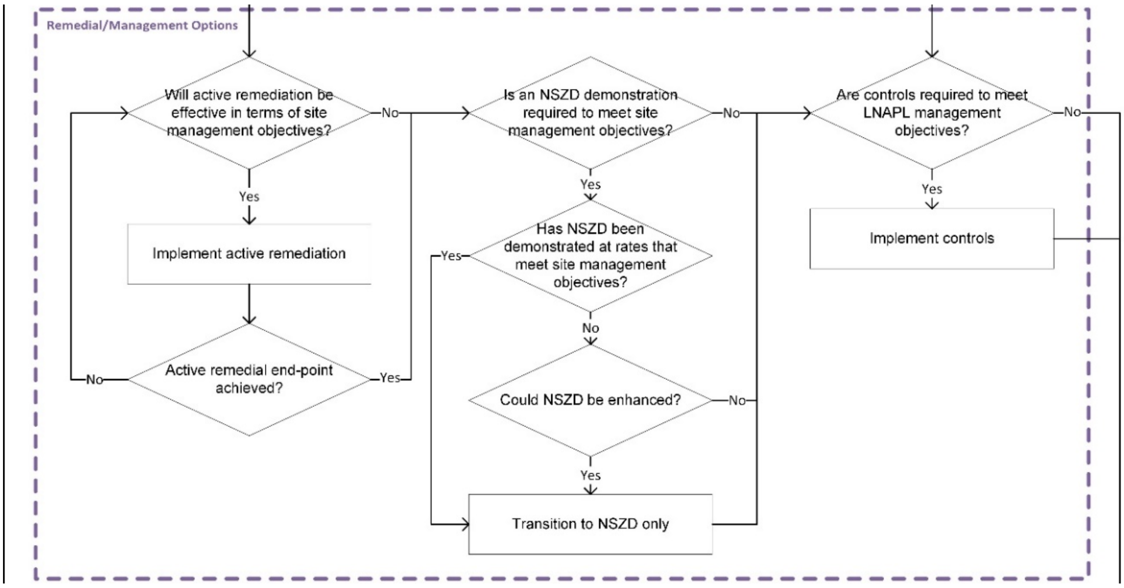

Figure 15: Remedial/management options assessment and implementation

The evaluation and implementation of remedial/management options will involve concurrent considerations of the need for active/engineered systems, NSZD, and/or controls as part of the overall LNAPL management strategy. LNAPL site management strategy can take different forms that will be dependent on the site management objectives identified following LCSM development and remedial options assessment. Even though an LNAPL management strategy is therefore necessarily site-specific, there are a finite number of scenarios that can exist at LNAPL sites with respect to different site conditions and corresponding potential technical remedial objectives and resulting strategies. A general guide is provided in Table 6 to assist with evaluating the applicability of potential components of an LNAPL remedial/management strategy. Table 6 lists eight scenarios that cover the range of possible technical remedial drivers that may exist at an LNAPL site b grouping the different possible combinations of saturation-based and compositional concerns and specifying the potentially applicable management approaches. The main function of Table 6 is to help focus the application of saturation reduction techniques where a saturation reduction/control driver is present and compositional/phase change techniques where a compositional change/control driver is present. Conversely, the use of Table 6 will help avoid the application of management strategies that are technically incompatible with the site-specific concerns. For example, Scenario 1 represents a site with concerns regarding both potential exposures and ongoing LNAPL mobility and migration. Therefore, active saturation reduction and compositional change techniques or related controls are applicable considerations. Conversely, Scenario 8 indicates a site in a late stage where there are no mobility or compositional exposure concerns. Therefore, no technical remedial drivers exist and no remedial techniques are specified on that basis. Overall, Table 6 will support the evaluation of remedial options in determining when active remedial techniques are likely to provide a potential technical benefit based on site conditions and corresponding technical drivers. For example, Table 6 helps focus when a driver for LNAPL recovery may exist (Scenarios 1, 2, 5 and 6), as well as when LNAPL recovery is unlikely to provide a technical benefit in terms of a measurable change in conditions (Scenarios 3, 4, 7 and 8).

Table 6: LNAPL management strategy matrix (adapted from Canadian Department of National Defence 2013)

(A) Possible LNAPL site concerns/technical remedial drivers					**(B)** Potential LNAPL site management options	
Scenario #	Compositional risk (dissolved or vapour phase risk) **Key indicators:** exceedance of risk-based criteria and complete or potentially complete pathways	LNAPL body migrating or expanding **Key indicators:** progressive expansion in extent of LNAPL in wells and/or expanding dissolved plume	Mobile LNAPL within stable LNAPL body **Key indicators:** LNAPL observed in wells with no evidence of LNAPL migration or expansion*	LNAPL recovery considered practicable **Key indicators:** LNAPL transmissivity *de minimis* criterion exceedance*	Active compositional change techniques and/or controls	Active saturation reduction (LNAPL mass recovery) techniques and/or containment
1	Yes	Yes	Yes	yes	✓	✓
2	Yes	No	Yes	yes	✓	✓
3	Yes	No	Yes	no	✓	✗
4	Yes	No	No	no	✓	✗
5	No	Yes	Yes	yes	✗	✓
6	No	No	Yes	yes	✗	✓
7	No	No	Yes	no	✗	✗
8	No	No	No	no	✗	✗

Notes: The technically appropriate remedial strategy **(B)** will be defined by the site-specific scenario of concerns **(A)**
Tables 5 and 8 provide additional metrics which may be applied in the evaluation of LNAPL mobility, recoverability and overall stability
✓ potentially applicable approach
✗ approach inconsistent with concern and/or unlikely to provide a technical benefit with respect to concern

Implicit in the overall LNAPL site management strategy (Figure 9) and Table 6 are the following considerations in the interest of developing an effective and sustainable LNAPL management strategy:

- Will active/engineered remedial techniques be effective (i.e. technically and cost-effective, implementable, result in a net environmental benefit) alone or as part of a treatment train approach?
- Are engineering or administrative controls (exposure pathway controls) required in addition to or in lieu of active/engineered remedial techniques?
- Is the confirmation and/or quantification of NSZD (including dissolved phase MNA) required to meet management objectives?
- What monitoring is needed to confirm management objectives are met?

Each of these considerations is contemplated further in the remainder of this section.

3.5.1 Engineered active remedies

The fundamental consideration at this stage will be that the capabilities of a given technique align with the identified LNAPL management objectives and related goals. This will serve to avoid the implementation of a remedial technique that is inconsistent with the objectives and will, therefore, be ineffective at reaching the specific management goals. For example, if a compositional objective relating to the mitigation of exposures associated with a dissolved plume is identified, the implementation of a saturation-based remedy such as conventional active LNAPL mass recovery techniques will not apply and will not be effective. In general, a saturation-reduction technique such as LNAPL mass recovery will be ineffective for a compositional objective unless most of the LNAPL can be recovered (e.g. by excavation or in-situ thermal). Similarly, a compositional change technique such as air sparge/soil vapour extraction (AS/SVE) will generally be considered inapplicable for a saturation-based objective since the goal will often be based on recovering LNAPL. Exceptions exist with certain approaches that can simultaneously achieve both saturation reduction and compositional change (e.g. bioventing, high vacuum multi-phase extraction, NSZD) and both types of objectives may be applicable at a given site. This scenario can be addressed through the selection of a single technique that can achieve the desired level of saturation and compositional change concurrently, or through a treatment train approach where multiple techniques are implemented consecutively. A comprehensive resource on potential remedial techniques including details on applicability, capabilities and other considerations is provided by ITRC (2018).

Typical considerations in the assessment of remedial options include technical effectiveness, cost effectiveness, and implementability. Another key consideration at this point will be the realistic potential net environmental benefit of the various remedial options including the principles of ecological sustainable development. The risk posed and the environmental footprint of remedial operations can be significant and should be weighed against the potential beneficial change in subsurface conditions. As discussed, LNAPL bodies will often be found to be stable (not migrating) with little potentially recoverable fraction. If the LNAPL does not pose a risk to receptors, or where exposures can be effectively controlled, there will be no technical benefit in the implementation of engineered active means in terms of reducing risk to receptors or migration potential that might balance the financial and environmental costs of the remedial activity. Table 7 provides an example of the implementation of a MPE system at a site where the LNAPL body had been in place for years and shown to be stable with low recoverability (i.e. *de minimis* LNAPL transmissivity). In this case, the potential exposures were mitigated through engineering and institutional controls (engineered cap and deed restrictions). Notwithstanding these considerations, the MPE system was implemented to address a regulatory objective to recover LNAPL to the maximum extent practicable based on the presence of significant in-well LNAPL thicknesses. Table 7 summarises the results of two years of MPE operation showing, amongst other things, that the greenhouse gas emission rate (based on the system's power consumption) exceeded the LNAPL recovery rate by three orders of magnitude. This provides an example of the importance of the consideration of net environmental benefit, particularly with systems that may be implemented based on objectives that are not connected to the mitigation of migration or risk potential.

Table 7: Implementation of an MPE system at a Superfund site where preceding testing indicated the LNAPL would be largely unrecoverable (i.e. *de minimis* LNAPL transmissivity). Financial and environmental costs are compared with system benefit following over 2 years of system operation. In this example, the LNAPL body was old/stable and all potential exposures were controlled. Average greenhouse gas (GHG) emission rate exceeded LNAPL recovery rate by three orders of magnitude (Rousseau 2015).

Benefit	LNAPL recovery	400 litres 360 kg 0.2 kg/hour
Costs	Financial	>\$1,000,000 >\$2,500/litre LNAPL >\$2,800/kg LNAPL
	GHG emissions – CO_2, CH_4, N_2O (based on electrical power consumption, US EPA eGRID emission factors)	>150,000 kg >100 kg/hour
	Environmental Footprint (based on US EPA SEFA spreadsheets, power consumption, manufacturing of materials, groundwater extraction, etc.)	143,000 kg CO_2e 7,300 kg NO_x+SO_x+PM 20 kg HAPs

CO_2e: CO_2 equivalents, NO_x: oxides of nitrogen, SO_x: oxides of sulphur, HAPs: hazardous air pollutants (carcinogens)

Inter-generational equity is a consideration in the management of LNAPL sites. This can be interpreted to mean that efforts must be made to get as much LNAPL out of the ground as practicable to limit the residual mass that remains into the future (e.g. consistent with a regulatory objective of restoring beneficial use of groundwater). However, the potential benefit of conventional active LNAPL recovery activities will be quite limited at many sites and petroleum LNAPL bodies will almost universally be expected to attenuate naturally through NSZD over time. Furthermore, as we can see in the example in Table 7, LNAPL recovery efforts may be associated with significant detrimental effects such as diminished air quality and the exacerbation of climate change. Intergenerational equity may be better maintained at many LNAPL sites if the realistic net environmental benefit of various management options is taken into account in the development of the LNAPL management strategy. While there will be instances when the potential benefit of active interventions is significant, particularly with recent releases and/or actively expanding LNAPL bodies, it should not be assumed that this is so. For example, in the example in Table 7, the benefit of a small fractional source reduction might be scrutinised considering the release of hazardous air pollutants and carbon footprint associated with the operation of the system. This can be an important decision-making factor that will most appropriately be assessed on a site-specific basis.

Once an active LNAPL remedial technology is implemented, the next consideration is when a practical endpoint has been reached. Endpoints for compositional objectives are usually fairly straightforward with target concentrations in the media of concern that must be achieved, which could involve the use of a single technology or more than one in sequence (i.e., treatment train approach). Remedial endpoints relating to saturation-based objectives and goals may involve a multiple lines of evidence approach. Table 8 provides options for demonstrating that a practical endpoint to a particular remedial technique has been reached. Regardless of whether the management objective is compositional or saturation-based, a consideration of the net environmental benefit of continuing a particular activity can be carried through as part of the ongoing evaluation of system performance over time.

As indicated by some of the end-point options listed in Table 8, achieving a practical endpoint to a given system's operation does not necessarily mean that the LNAPL management objectives have been met. Once a practical endpoint is reached for a given engineered remedial activity or combination of technologies, the decision-making framework prompts consideration of the following:

- Whether engineering or administrative controls are required to meet the LNAPL site management objectives.
- Whether it is appropriate to allow NSZD to achieve the management objectives over a longer time frame.

3.5.2 Controls

Controls will be common components of an LNAPL management strategy that may be implemented with or without a preceding engineered active remedial stage. The basic types of controls are commonly categorised as follows:

- **Institutional controls** are a form of land use control that provides protection from exposure to contaminants (ITRC 2016). Institutional controls typically take the form of administrative procedures (e.g. site-specific health and safety plan) or legal instruments (e.g. deed restrictions).
- **Engineering controls** are infrastructure designed to mitigate exposures by limiting the extent of contaminants (e.g. physical containment) and/or interrupting the exposure pathway (e.g. sub-slab depressurisation system).

Conventional active LNAPL remedial technologies may be impracticable and/or will not provide a net environmental benefit at many LNAPL sites. In this situation, controls have the potential to offer a more effective and sustainable approach to LNAPL site management that may also provide an improved net environmental benefit overactive approaches.

Table 8: Potential endpoints to active engineered remedial efforts. Note that certain parameters such as LNAPL transmissivity and NSZD rates may vary temporally/seasonally.

Objective	Threshold criteria	Potential endpoint
Saturation-based		
Mitigate LNAPL body migration potential (stabilise LNAPL body)	Multiple lines of evidence indicate LNAPL body migration or expansion (see Appendix C)	1. Multiple lines of evidence indicate the LNAPL mobility potential has been reduced such that the LNAPL body is stable 2. Further saturation-reduction is deemed to be impracticable as determined via one or more of the practical limits/endpoints shown below
Recovery to a practical limit	LNAPL thickness in wells	One or more of: 1. LNAPL transmissivity demonstrated to be mostly or completely <0.08 m^2/day (0.8 ft^2/day) 2. LNAPL saturations are demonstrated to be mostly or completely at residual levels 3. Decline curve* indicates less than 10% of the potentially recoverable LNAPL remains 4. NSZD rates are comparable to or exceed system performance 5. Further system operation will not provide a net environmental benefit
Compositional		
Mitigate unacceptable health or ecological exposures	Exceedance of generic regulatory criteria and potentially complete exposure pathway Results of quantitative HERA indicates unacceptable exposure potential	1. Target concentrations are achieved at points of compliance 2. Further reductions in target constituent concentrations are deemed to be impracticable 3. Further system operation will not provide a net environmental benefit 4. Controls will provide more effective risk mitigation

*Example decline curve analysis is provided in Appendix D

3.5.3 Natural source zone depletion

As previously mentioned, the assessment of NSZD can be useful in both LCSM development and remedial options assessment to establish what baseline LNAPL degradation rates are, and to understand the potential net benefit of engineered systems over NSZD alone. Since NSZD is actively degrading LNAPL, it also constitutes an LNAPL management option in and of itself. As summarised by CL:AIRE (2019), NSZD processes may:

- Significantly reduce LNAPL mass, LNAPL saturation levels and, therefore, the ability for LNAPL to migrate and/or be recovered over time.

- Allow the development of a more precise and comprehensive LCSM that includes all key physical, chemical, and biological processes that control contaminant transport and potential impacts.
- Progressively reduce contaminant fluxes that may sustain both subsurface vapour and groundwater plumes thereby leading to reduced receptor risks and gradual plume shrinkage.
- Influence the timeframes over which plume remediation options such as MNA or other in situ technologies need to be employed to protect receptors.
- Influence decision making on the need for active remediation technologies that may deliver faster (but partial) source zone removal, but may not generate significant risk-reduction when compared to NSZD processes alone (adapted from CL:AIRE 2019).

NSZD may also offer the following advantages over other options:

- It will produce less environmental impact than engineered techniques.
- It is not subject to the same limitation as conventional active LNAPL recovery means in only accessing the mobile/recoverable fraction of an LNAPL body.
- It will be a lower cost option than many engineered systems.

NSZD therefore offers the benefit of continued source zone depletion when more conventional active LNAPL recovery methods are deemed to be ineffective a priori or where a practical limit to their effectiveness has been reached. Accordingly, NSZD could serve as the primary remedial approach or as a secondary long-term option following the implementation of engineered approaches when the following conditions are met:

- The LNAPL body has stabilised.
- LNAPL recovery is infeasible and/or will not provide a beneficial change in conditions (i.e. one or more of the saturation-based endpoint metrics in Table 8 apply).
- There are no potentially unacceptable risks to human health or the environment, or potential risks can be effectively mitigated through controls.

Where these conditions are met, the implementation of conventional active LNAPL recovery techniques can be considered to be impracticable since the activity will not achieve a useful LNAPL saturation/mass/volume reduction and, therefore, no net environmental benefit. NSZD would be an applicable consideration at this point whether or not an engineered system is implemented.

3.6 Long-term monitoring

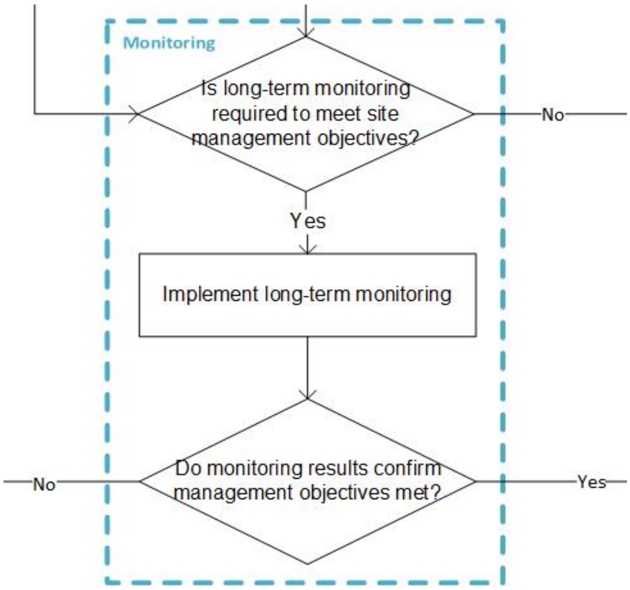

Figure 16: Long-term monitoring consideration in the LNAPL management strategy

Some long-term monitoring is likely to be required to confirm LNAPL management objectives have been met, including confirmation of LCSM aspects such as ongoing LNAPL body/dissolved plume stability and the absence of any unacceptable health and environmental risks. A number of conditions can, and likely do, vary seasonally/ temporally at LNAPL sites including LNAPL mobility, recoverability, NSZD rates, as well as dissolved and vapour phase concentrations. Variations in temperature, rainfall and groundwater levels may affect these conditions. The appropriate timeframe and frequency of monitoring will typically be site specific and subject to jurisdictional policy requirements; therefore, practitioners should refer to the regulatory documentation relevant to the site. With respect to NSZD monitoring specifically, CRC CARE Technical Report 44 provides guidance on test methods and best practices in their implementation.

4. Case studies

Eight case studies are provided in Appendix E, with a summary discussion provided in this section. The case studies include both Australian and overseas sites in order to provide a selection of different LNAPL management strategies and to illustrate different ways that NSZD was monitored and utilised in the respective strategies. The case studies cover a range of LNAPL types and geologies including both lighter (more volatile) and heavier (less volatile) product types in both soil and fractured rock settings. A summary of the maximum NSZD rate estimates and monitoring methods from the case study sites is provided in Table 9.

The case studies support the ubiquity of NSZD in that it was observed to be active at all subject sites, regardless of LNAPL type or environmental setting. The results suggest that the estimated NSZD rates can be method-dependent with the majority of case study sites exhibiting NSZD rate estimates that varied by up to an order of magnitude amongst the methods employed. Conversely, there was general agreement on the order of magnitude of the NSZD estimates for half the sites investigated here. It is noted that the methods are measuring NSZD different ways over different timeframes, so some variability is to be expected. It is also likely that certain methods will be more applicable/accurate at certain types of sites compared to others. For example, surficial CO_2 efflux-based methods may work very well at certain sites (e.g. porous media, unsealed surface cover). However, the technique can easily miss a significant portion of the petrogenic CO_2 at more complex sites (e.g. complex stratigraphy, fractured rock) if sample locations are not ideally targeted, which will result in NSZD rates being biased low. In addition, the use of surficial techniques at sites with impermeable surface cover can result in significant positive bias in NSZD rate estimates due to preferential soil gas flow through perforations made for sampling. That said, the reasons for the variability observed at some of the case study sites is not yet well understood. CRC CARE Technical Report 44 provides detailed information on the different methodologies, their applicability, as well as current best practices in their implementation and the associated NSZD rate estimations. In addition, CSIRO continues to trial different methods concurrently at several Australian sites in an effort to refine best practices in both the quantification of NSZD and application/development of NSZD modelling. In general, method selection is not a trivial matter and it may be necessary to use multiple methods at a given site to confirm and quantify NSZD since the evidence of NSZD can be subtle/difficult to detect depending on the method employed.

Table 9: Summary of case study reported NSZD rates and methods

Case study	Setting	Maximum observed NSZD rate (L LNAPL ha^{-1} yr^{-1})	Monitoring method(s)[a]	Monitoring method producing maximum NSZD rate estimate	Notes
1	Condensate in limestone (Australia)	87,000	1, 2, 3, 4, 5	5	Methods varied up to a factor of 10
2	Diesel, crude oil in sand (Australia)	17,000	1, 3, 4	4	General agreement (order of magnitude) among methods
3	Diesel, gasoline in fractured sedimentary rock (Australia)	8,800	3, 4	3	Methods varied up to a factor of 10
4	Jet fuel in sand (Australia)	179,000	1, 2	1	General agreement (order of magnitude) among methods
5	Diesel in weathered/ fractured rhyodacite (Australia)	20,000	1, 2, 3	1	All methods agreed within a factor of 2
6	Diesel in interbedded sands and clays (USA)	187,000	1, 2	1	Spatially weighted average DCC estimates exceeded Trap estimates by a factor of 10
7	Gasoline with minor diesel and lube in weathered and fractured basalt	5,100	2, 3, 4	3	Temporal within method variation is similar in magnitude to variations between methods
8	Diesel and minor lube oils in weathered fractured basalt	13,000	2, 3	3	Temporal within method variation is similar in magnitude to variations between methods

[a]Methods: 1) surficial CO_2 efflux via dynamic closed chamber (DCC), 2) surficial CO_2 efflux via passive CO_2 traps, 3) biogenic heat/temperature, 4) subsurface soil gas sampling/ profiling, 5) LNAPL compositional change.

Active LNAPL recovery was operating at all but one site (site 5) investigated here. While this site did not have a history of LNAPL recovery, potentially recoverable LNAPL was not observed to accumulate in wells and, therefore, potential LNAPL recovery rates are assumed to be negligible (i.e. *de minimis* LNAPL recoverability). In all cases, estimated NSZD rates by some methods exceeded active LNAPL recovery performance. At the seven case study sites where NSZD rate estimates and active LNAPL recovery system performance could be compared directly, mass losses from NSZD were up to 50-times[7] greater than the LNAPL mass recovery being achieved by the active systems.

In order to perform this comparison, it is necessary to estimate the area over which NSZD is active and project the NSZD measurements across this area to estimate LNAPL body-wide mass losses from NSZD. NSZD is assumed to be active across the overall LNAPL body footprint, which can be confirmed on a site-specific basis via NSZD monitoring results. Therefore, the area of focus for the overall NSZD rate estimate is the entire LNAPL body extent.[8] Since conventional active LNAPL mass recovery activities will typically be unable to have any effect on residual LNAPL, the area of focus for active systems is limited to the accessible area(s) containing mobile LNAPL in wells. It would therefore be incorrect to project LNAPL recovery rates for a given area of mobile LNAPL across the wider overall LNAPL body extent.

The case studies show that typical NSZD monitoring events will result in data from multiple locations across a given LNAPL body extent. In order to determine a spatially-weighted average NSZD rate that can be applied to a given LNAPL footprint, the case studies employ a Theissen polygon approach to determine a spatially-weighted average NSZD rate that, when applied to the LNAPL body footprint/area, allows direct comparison of NSZD rates to LNAPL mass recovery performance (in units of volume or mass per time). A number of case studies, including case studies 6 and 8 provide graphical examples of this approach, which is also shown in CRC CARE Technical Report 44 (CRC CARE 2018) and Rayner *et al* (2020). Overall, the case studies:

- Support the ubiquity of NSZD in that it was confirmed to be occurring at all case study sites.
- Suggest a method-dependency to NSZD rate estimates at some sites that will be investigated further through ongoing work at test sites in Australia.
- Illustrate a method that can be used to convert NSZD rates in the typical units of volume area^{-1} time^{-1} (e.g. L LNAPL ha^{-1} yr^{-1}) to volume time^{-1} or mass time^{-1} units (e.g. L yr^{-1} or tonnes yr^{-1}) for more direct comparison to active LNAPL recovery rates.
- Indicate that NSZD rates can substantially exceed active LNAPL recovery rates and, therefore, that the net environmental benefit of continued active system operation should be assessed on an ongoing basis.
- Show a number of ways NSZD monitoring data can be used including in supporting the evaluation of LNAPL body stability, assessing the potential benefit

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[7] *Part of this range is due to the variability observed in some of the method-specific NSZD rate estimates at some of the sites.*

[8] *Appendix B details site information that can be used to estimate overall LNAPL body extent including areas of mobile LNAPL where it is observed in wells and areas of residual LNAPL where it may not be observed in wells.*

of active LNAPL mass recovery, and as a component of the overall LNAPL management strategy.

It is noted that the NSZD monitoring methodologies are not described in detail in the case studies. The reader is directed to CRC CARE Technical Report 44 for more comprehensive information on NSZD monitoring and the development of NSZD rate estimates.

5. Conclusions

A consideration of the potential role of NSZD in LNAPL site management is becoming increasingly viewed as relevant to the effective and sustainable management of LNAPL sites. There are different roles that NSZD can play in the site management process as NSZD can:

- Significantly reduce LNAPL mass, LNAPL saturation levels and, therefore, the ability for LNAPL to migrate and/or be recovered over time.
- Allow the development of a more precise and comprehensive LCSM that includes all key physical, chemical, and biological processes that control contaminant transport and potential impacts.
- Progressively reduce contaminant fluxes that may sustain both subsurface vapour and groundwater plumes thereby leading to reduced receptor risks and gradual plume shrinkage.
- Influence the timeframes over which active plume remediation options need to be employed to protect receptors.
- Influence decision-making on the need for active remediation technologies that may deliver faster (but incomplete) source zone removal, but may not generate significant risk-reduction when compared to NSZD processes alone (adapted from CL:AIRE 2019).

This report provides a framework illustrating how consideration of NSZD naturally fits into different stages of an overall science and risk-based LNAPL management strategy including:

- **During LCSM development** as a baseline evaluation of LNAPL degradation, and to better understand and support conclusions regarding LNAPL stability.
- **During remedial options assessment** as a component of a remedial/management strategy, and to better understand the incremental benefits of active LNAPL recovery compared with the NSZD.
- **During remediation/management** as a primary LNAPL management technique, as a secondary approach following active recovery methods, and/or as a consideration when assessing whether an acceptable endpoint to active remediation has been reached. Since NSZD is a ubiquitous naturally occurring phenomenon, it will be part of all LNAPL site management strategies by default. As a standalone remedy, NSZD will be most applicable where LNAPL is stable, LNAPL recovery is technically impracticable and/or will not provide a benefit, and there are no potential exposures (or exposures can be effectively mitigated with controls).

The case studies presented provide a number of insights regarding NSZD in general and NSZD at Australian sites specifically. Key observations include the apparent ubiquity of NSZD and the potential significance of NSZD rates. It is notable that the case studies indicate that NSZD rates observed at Australian sites are comparable or exceed what is considered typical overseas. Additionally, the case studies indicate that NSZD is substantially outperforming conventional active LNAPL recovery performance at all sites where the comparison was possible (i.e. where active LNAPL recovery efforts were taking place).

The study of NSZD is an area of active research, particularly with respect to the refinement of monitoring methods, best practices in their implementation, and longer-term studies that might be used to project NSZD rate trends over time and develop related modelling applications. In an attempt to address these needs, ongoing studies at Australian sites by CSIRO using multiple monitoring methodologies concurrently with different LNAPL types in different settings are underway.

6. References

Adamski, M, Kremesec, V & Charbeneau, RJ 2003, *Residual saturation: What is it? How is it measured? How should we use it?*, United States Environmental Protection Agency Technology Innovation and Field Services Division, Contaminated Site Clean-up Information (CLU-IN) forum, <www.clu-in.org/conf/itrc/iuLNAPL/030513_residual.pdf>.

American Petroleum Institute (API) 2004, *API interactive LNAPL guide version 2.0.4,* API Regulatory and Scientific Affairs Department, Washington DC, USA.

API 2017, *Quantification of vapor phase-related NSZD processes*, Publication No. 4784, Washington DC, USA.

API 2018, *Managing Risk at LNAPL Sites: Frequently Asked Questions*, Soil and Groundwater Research Bulletin No. 18, Washington DC, USA.

ASTM International 2014, *Standard guide for development of conceptual site models and remediation strategies for light nonaqueous-phase liquids released to the subsurface,* E2531-06(2014), Pennsylvania, USA.

Beck, P & Mann, B 2010, *A technical guide for demonstrating monitored natural attenuation of petroleum hydrocarbons in groundwater*, CRC CARE Technical Report no. 15, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Canadian Department of National Defence 2013, *A management framework for LNAPL sites at 5 Wing Goose Bay*, Happy Valley-Goose Bay, Newfoundland, Canada.

Clements, L, Palaia, T & Davis, J 2009, *Characterisation of sites impacted by petroleum hydrocarbons: National guideline document*, CRC CARE Technical Report no. 11, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Connor, JA, Kamath, R, Walker, KL & McHugh, TE 2015, Review of quantitative surveys of the length and stability of MTBE, TBA and benzene plumes in groundwater at UST sites, *Groundwater*, vol. 53, no. 2, pp. 195–206.

Contaminated Land: Applications in Real Environments (CL:AIRE) 2014, *An illustrated handbook of LNAPL transport and fate in the subsurface*, CL:AIRE, London, UK.

CL:AIRE 2019, *Technical bulletin 20: an introduction to natural source zone depletion at LNAPL sites*, CL:AIRE, London, UK.

CRC CARE 2013, *Petroleum hydrocarbon vapour intrusion assessment: Australian guidance*, CRC CARE Technical Report no. 23, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

CRC CARE 2015, *A practitioner's guide for the analysis, management and remediation of LNAPL*, CRC CARE Technical Report no. 34, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

CRC CARE 2017, *Weathered Petroleum Hydrocarbons (Silica Gel Clean-up)*, CRC CARE Technical Report no. 40, CRC for Contamination Assessment and Remediation of the Environment, Newcastle, Australia.

CRC CARE 2018, *Technical measurement guidance for LNAPL natural source zone depletion*, CRC CARE Technical Report no. 44, CRC for Contamination Assessment and Remediation of the Environment, Newcastle, Australia.

CRC CARE 2020, *National Remediation Framework.* The Framework comprises 24 modules, and is in draft as at April 2019, CRC for Contamination Assessment and Remediation of the Environment, Newcastle, Australia.

Davis, GB, Merrick, N & McLaughlan, R 2006, *Protocols and techniques for characterizing sites with subsurface petroleum hydrocarbons – a review*, CRC CARE Technical Report no. 2, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Davis, GB, Patterson, BM & Trefry, MG 2009, *Biodegradation of petroleum hydrocarbon vapours*, CRC CARE Technical Report no. 12, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Davis, GB, Trefry, MG & Patterson, BM 2009, *Pet,roleum vapour model comparison*, CRC CARE Technical Report no. 9, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia

Davis, GB, Wright, J & Patterson, BM 2009, *Field assessment of vapours*, CRC CARE Technical Report no. 13, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Friebel, E & Nadebaum, P 2007, *The development of HSLs for petroleum hydrocarbons – an issues paper*, CRC CARE Technical Report no. 4, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Friebel, E & Nadebaum, P 2011, *Health screening levels for petroleum hydrocarbons in soil and groundwater*, CRC CARE Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Garg, S, Newell, CJ, Kulkarni, PR, King, DC, Adamson, DT, Renno, MI & Sale, T 2017, ‘Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change’, *Groundwater Monitoring & Remediation*, vol. 37, no. 3, pp. 62–81.

Hardisty, PE 2010, ‘The Economics of Remediating NAPLs in Fractured Aquifers’, in *Environmental and economic sustainability*, CRC Press, Boca Raton, Florida, USA.

Hawthorne, JM, Helsel, D & Stone, C 2015, ‘Nationwide (USA) statistical analysis of LNAPL transmissivity (T_n)’, sponsored by The American Petroleum Institute, poster presented at the Battelle Bioremediation Symposium, Miami, Florida, USA.

Huntley, D & Beckett, GD 2002, ‘Persistence of LNAPL sources: relationship between risk reduction and LNAPL recovery’, *Journal of Contaminant Hydrology*, vol. 59, no. 1–2, pp. 3–26.

Interstate Technology & Regulatory Council (ITRC) 2009, *Evaluating LNAPL remedial technologies for achieving project goals*, LNAPL-2, Interstate Technology & Regulatory Council, LNAPLs Team, Washington, USA.

ITRC 2014, *Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management*, PVI-1, Interstate Technology & Regulatory Council, L Petroleum Vapor Intrusion Team, Washington, USA, <www.itrcweb.org/PetroleumVI-Guidance>.

ITRC 2016, *Long-term contaminant management using institutional controls*, IC-1, Interstate Technology & Regulatory Council, Long-Term Contaminant Management Using Institutional Controls Team, Washington, USA, <institutionalcontrols.itrcweb.org/>.

ITRC 2017, *Characterization and remediation in fractured rock*, FracRx-1, Interstate Technology & Regulatory Council, Fractured Rock Team, Washington, USA, <www.itrcweb.org/fracturedRx-1>.

ITRC 2018, *Light non-aqueous phase liquid (LNAPL) site management: LCSM evolution, decision process and remedial technologies*, LNAPL-3, Interstate Technology & Regulatory Council, LNAPL Update Team, Washington, USA.

Johnston, CD 2010, *Selecting and assessing strategies for remediating LNAPL in soil and aquifers*, CRC CARE Technical Report no. 18, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Kamath, R, Connor, JA, McHugh, TE, Nemir, A, Le, MP & Ryan, AJ 2011, 'Use of long-term monitoring data to evaluate benzene, MTBE, and TBA plume behavior in groundwater at retail gasoline sites', *Journal of Environmental Engineering*, vol. 138, no. 4, pp 458–469.

Lundegard, PD & Johnson, PC 2006, 'Source zone natural attenuation at petroleum hydrocarbon spill sites – II: Application to a former oil field', *Ground Water Monitoring & Remediation*, vol. 26, no. 4, pp. 93–106.

Mace, RE, Fisher, RS, Welch, DM & Parra, SP 1997, Extent, mass, and duration of hydrocarbon plumes from leaking petroleum storage tank sites in Texas, Bureau of Economic Geology, Geologic Circular 97-1, University of Texas at Austin, Austin, Texas, USA.

Mahler, N, Sale, T & Lyverse, M 2012, 'A mass balance approach to resolving LNAPL stability', *Ground Water*, vol. 50, no. 6, pp. 861–871.

McLaughlan, RG, Merrick, NP & Davis, GB 2006, *Natural attenuation: a scoping review*, CRC CARE Technical Report no. 3, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Molins, S, Mayer, KU, Amos, RT & Bekins, BA 2010, 'Vadose zone attenuation of organic compounds at a crude oil spill site – Interactions between biogeochemical reactions and multicomponent gas transport', *Journal of Contaminant Hydrology,* vol. 112, no. 1, pp. 15–29.

Newell, CJ & Connor, JA 1998, *Characteristics of dissolved petroleum hydrocarbon plumes: Results from four studies*, American Petroleum Institute Soil and Groundwater Bulletin, Washington DC, USA.

Rayner, J, Bekele, E, Donn, M, Bastow, T, Davis, G, Woodbury, R, Furness, A & Geste, Y 2020, *Australian case studies of light non-aqueous phase liquid (LNAPL) natural source zone depletion rates compared with conventional active recovery efforts*, CRC CARE Technical Report no. 47, CRC for Contamination Assessment and Remediation of the Environment, Newcastle, Australia.

Rice, DW, Grose, RD, Michaelsen, JC, Dooher, B, MacQueen, DH, Cullen, SJ, Kastenberg, WE, Everett, LG & Marino, MA 1995, *California leaking underground fuel* *tank (LUFT) historical case analyses*, Environmental Protection Department, Environmental Protection Division, Lawrence Livermore National Laboratory, Livermore, California, USA.

Rousseau, M 2015, 'Innovative LNAPL conceptual site model development tools in support of more sustainable risk-based LNAPL site management', presented at the 6th International Contaminated Site Remediation Conference (CleanUp), Melbourne, Australia.

Sookhak Lari, K, Davis, GB, Rayner, JL, Bastow, TP & Puzon, GJ 2019, 'Natural source zone depletion of LNAPL: a critical review supporting modelling approaches', *Water Research*, vol. 157, pp. 630–646.

Suthersan, S, Koons, B & Schnobrich, M 2015, 'Contemporary management of sites with petroleum LNAPL presence', *Groundwater Monitoring & Remediation*, vol. 35, no. 1, pp. 23–29.

Tuczynowicz, L & Robinson, N 2008, *Review of current international approaches to total petroleum hydrocarbon assessment*, CRC CARE Technical Report no. 8, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

U.S. Army Corps of Engineers (USACE) 1999, *Multi-phase extraction – Engineering manual*, EM 1110-1-4010, U.S. Army Corps of Engineers, Washington, USA.

U.S. Environmental Protection Agency (US EPA) 2015, *Technical guide for addressing petroleum vapor intrusion at leaking underground storage tank sites*, EPA 510-R-15-001, Office of Underground Storage Tanks, Washington, USA.

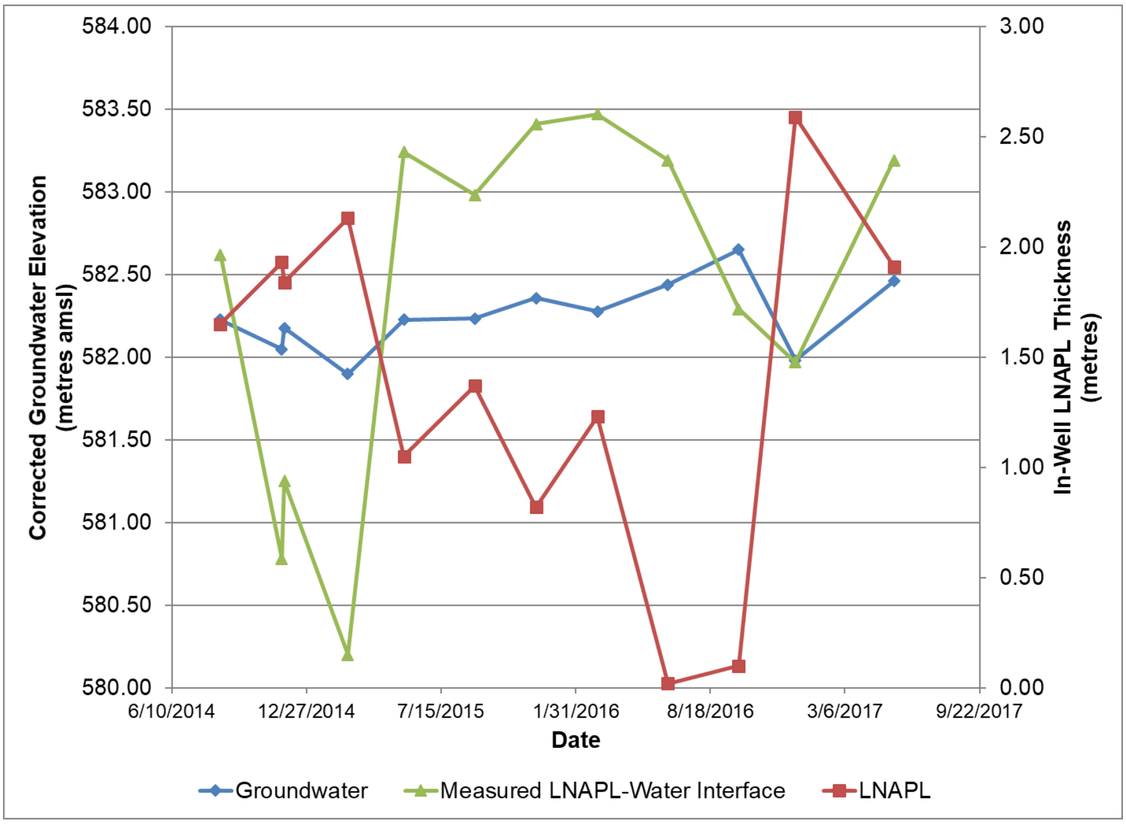
APPENDIX A.

Interpreting in-well LNAPL thickness

The misinterpretation of well gauging data remains a regular occurrence at LNAPL sites. Whilst in-well LNAPL thickness observations and trends can be meaningful in certain instances, the significance of the data is often overstated and can lead to poor LNAPL management decision-making. The following points will typically hold at most LNAPL sites (API 2018; CL:AIRE 2014; CRC CARE 2015; ITRC 2018):

- **Before LNAPL body stabilisation (new or recent release)**: in-well thickness changes can be, but are not necessarily, indicative of LNAPL body migration/expansion. For example, new and/or increasing trends in in-well LNAPL thickness in a well that was installed at a location with no evidence of petroleum impact, especially if preceded by new/increasing dissolved phase petroleum hydrocarbon concentrations, likely indicates a migrating/expanding LNAPL body. It is noted that low mobility LNAPL can result in an extended period of time for LNAPL to appear and accumulate in a newly installed well, which can also produce an increasing trend in in-well thickness. However, in this case, there will usually be evidence from field screening of soil borings or soil analytical results of the existence of petroleum contamination at a given location.
- **After stabilisation (older/mature LNAPL body)**: conversely, in-well LNAPL thickness changes after LNAPL body stabilisation are more likely localised LNAPL mobility that correlates with water table fluctuations. This localised LNAPL movement in and out of wells in response to changes in water table elevation will not contribute to LNAPL body migration or expansion. In-well thickness changes at this point will most often result from localised redistribution of LNAPL into and out of a well in response to water table elevation when/where LNAPL saturations exceeding residual levels exist. It is typical for LNAPL to be observed in wells within the confines of a stable LNAPL body. It is also typical that the magnitude of in-well LNAPL thickness will be variable and mostly controlled by water table elevation for a given setting and well construction scenario. If the LNAPL has been in the ground on a timescale of years and/or other lines of evidence indicate a stable LNAPL body, it is very unlikely that these observations will be indicative of LNAPL migration. Examples of natural variability in in-well LNAPL thickness within stable LNAPL bodies are provided in Figure A1.

With the exception of recent releases, the magnitudes and trends in in-well LNAPL thickness at most LNAPL sites have little to do with LNAPL migration potential (ITRC 2018). Similarly, in-well LNAPL thickness will typically be a poor predictor of the mobility and recoverability of the LNAPL (API 2018; CL:AIRE 2015; CRC CARE 2015; Hawthorne *et al* 2015; ITRC 2018). Most older LNAPL sites will have only a small fraction of the overall LNAPL volume that is potentially hydraulically recoverable. However, these sites can also exhibit large in-well LNAPL thicknesses. Conversely, wells with relatively small in-well LNAPL thickness can be associated with high LNAPL recoverability. Therefore, the presence of large in-well LNAPL thicknesses is not a reliable indicator that a significant fraction of the LNAPL body is recoverable any more than smaller in-well thicknesses can be assumed to represent a lack of recoverability. To illustrate, Figure A2 shows a plot of the results of approximately one thousand T_n tests against the respective pre-test in-well LNAPL thickness. As shown in Figure A2, there is no correlation between LNAPL recoverability (as defined through standardised T_n test results) and the magnitude of in-well LNAPL thickness. Some of the lowest LNAPL transmissivities were noted in wells with some of the highest pre-test in-well thicknesses, and vice versa.



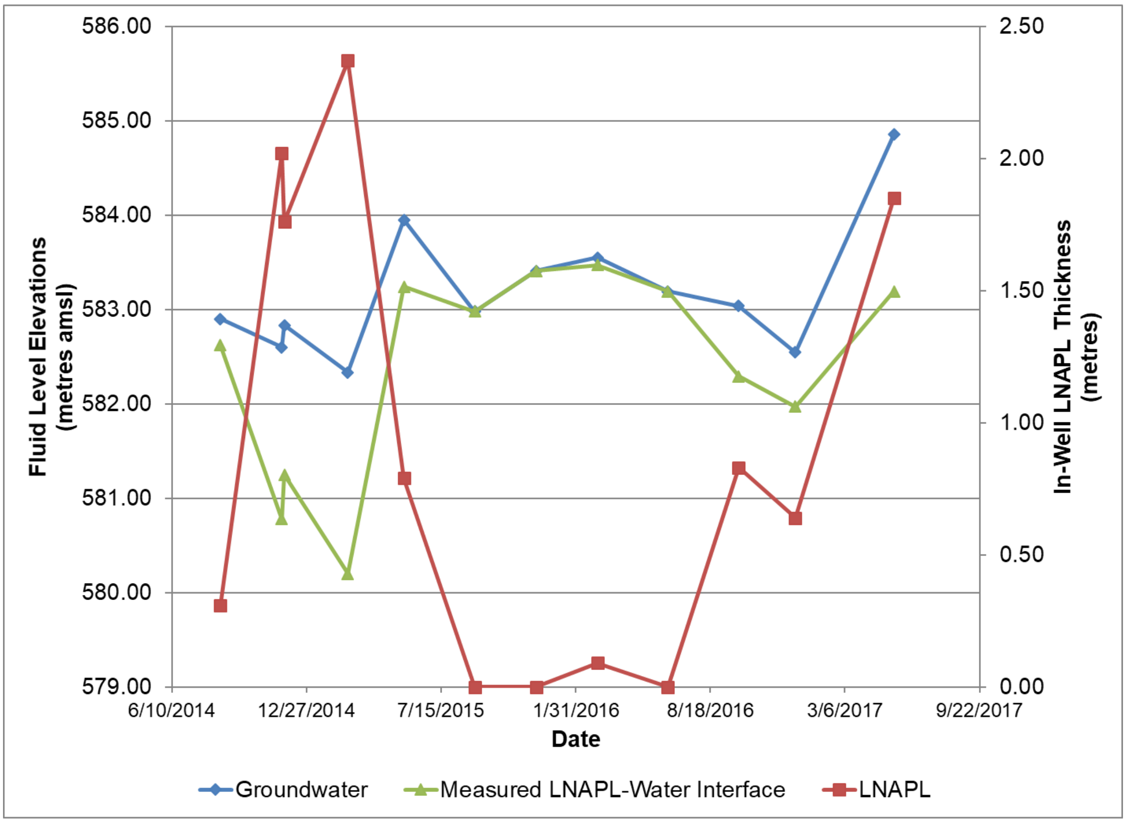


Figure A1: Typical examples of fluctuating in-well LNAPL thickness in both unconfined (top) and mixed unconfined/confined (bottom) settings in stable LNAPL bodies. In-well LNAPL thickness varies inversely with changes in water table elevation in unconfined conditions. In confined conditions, there is a direct relationship between in-well LNAPL thickness and potentiometric surface elevation (more pressure, more LNAPL pushed into the well). Both conditions can be observed at different times at a given location due to different water table conditions (provided by GHD).

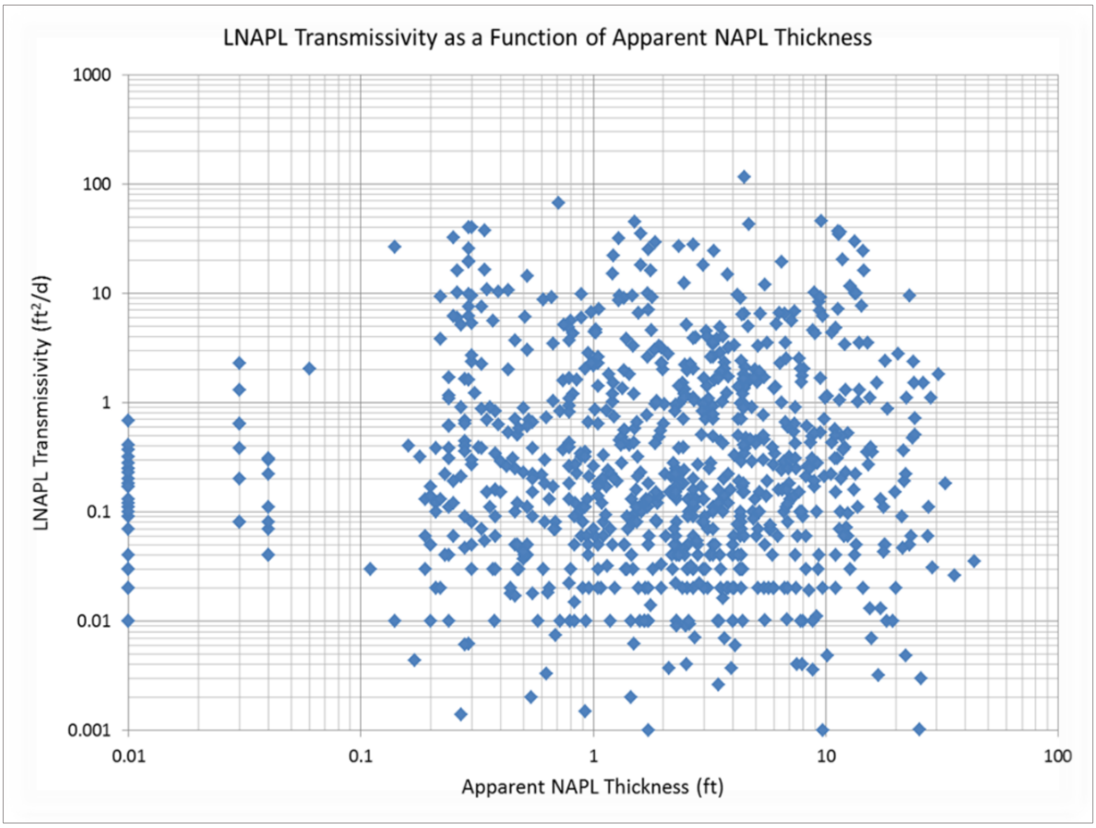


Figure A2: Comparison of LNAPL transmissivity estimates and pre-test in-well LNAPL thickness for approximately one thousand test results (Hawthorne *et al* 2015).

Well gauging data are most useful as a component of an LCSM that can help define where LNAPL saturations exceed residual (i.e. the mobile LNAPL extent) and the hydrogeological conditions that the LNAPL exists under. However, getting to reliable answers on whether LNAPL is migrating, how much of it might be recoverable, and whether hydraulic recovery might be considered practicable will require a multiple lines of evidence approach and cannot be answered solely through the interpretation of in-well LNAPL thickness data. Since in-well LNAPL thickness does not provide a reliable indicator of LNAPL recoverability, it follows that it does not constitute a reliable threshold or end-point metric for LNAPL recovery activities (API 2018; CL:AIRE 2015; CRC CARE 2015; Hawthorne *et al* 2015; ITRC 2018).

KEY POINTS:

In-well LNAPL thickness data/observations are most useful as:

- **indicators of the extent of mobile LNAPL (where saturations exceed residual) within the overall footprint of an LNAPL body, and**
- **a diagnostic tool for the identification of the hydrogeologic condition the LNAPL is present under.**

In-well LNAPL thickness data/observations are least useful as:

- **indicators of the magnitude of LNAPL mobility/recoverability**
- **threshold or end-point metrics for LNAPL mass recovery activities, and**
- **indicators of remedial progress.**

APPENDIX B.

Potential LNAPL indicators

Potential LNAPL indicators (adapted from ITRC 2018)

Media/Zone	Indicator	Notes
Groundwater	Current or historical LNAPL presence (including sheens)	Consider groundwater levels and well construction details along with observations of in-well LNAPL presence/thickness to provide correct interpretations.
	Constituent concentrations approach/exceed effective solubilities	Effective solubilities can be calculated on a site-specific basis if LNAPL composition is known or literature sources can be used (e.g. API 2004). Other potential indicator concentrations referenced in the literature (summarised in ITRC 2018): Benzene > 1–5 mg/L $TPH_{(gasoline)}$ > 30 mg/L BTEX > 20 mg/L
Soil	Ultraviolet (UV) or laser-induced fluorescence (LIF) above background levels	Indicates the presence of LNAPL.
	Current or historical LNAPL presence (including sheens, staining)	Indicates the presence of LNAPL.
	TPH or constituent of concern (COC) concentrations indicate C_{sat} exceeded or LNAPL saturation	Can be compared to theoretical C_{sat} or converted to LNAPL saturation. Other potential indicator concentrations referenced in the literature (summarised in ITRC 2018): $TPH_{(gasoline)}$ > 250–500 mg/kg $TPH_{(diesel)}$ > 10–30 mg/kg
	Visible fluorescence in UV core photography	Typical component of petro physical test programs.
	Core sample exhibits measurable LNAPL saturation	Typical component of petro physical test programs.
	Shake test indicates LNAPL presence	Soil sample placed in water and shaken to test for visible sheen/LNAPL, may be used with lyophilic dye to stain produced LNAPL for ease of detection (e.g. OilScreenSoil®).
Vapour/ soil gas/vadose zone	Elevated photoionisation detector (PID) or flame iodinasation detector (FID) screening results	May be appropriate for recent releases of volatile LNAPL types. Older or less volatile LNAPL types may produce little or no PID/FID reading.
	Gaseous NSZD by products or temperature anomalies in vases zone	Evidence of NSZD indicates the presence of LNAPL.

APPENDIX C.

Potential lines of evidence for LNAPL mobility, recoverability and overall stability

Potential lines of evidence for LNAPL mobility, recoverability and overall stability

Parameter	Potential lines of evidence	Notes
Stability	LNAPL age (time since release)	The longer the LNAPL has been in the ground, the more likely it is that it will have naturally stabilised.
	Well observations	Focus on areal extent of LNAPL observations in wells over time. Recall that well-specific trends in in-well LNAPL thickness will not be reliable indicators of LNAPL migration at many sites. Exceptions that warrant further consideration include LNAPL appearance in a well that was installed in clean soil, especially if preceded by increasing dissolved phase concentrations, or increasing in-well LNAPL thickness that does not appear to correlate with water table fluctuations.
	Trends in dissolved phase extent, dissolved mass, centre of mass location	A holistic plume-scale approach to evaluating dissolved plume stability is preferred over well-specific trend analysis at LNAPL sites, which can often produce confounding and/or inconclusive results. A stable dissolved phase indicates the same must be true of the LNAPL source material.
	LNAPL mobility lines of evidence	One or more LNAPL mobility lines of evidence indicating wide-spread mobility or mobility along the LNAPL body periphery may indicate LNAPL migration potential. Recall that the LNAPL body periphery may not be defined by where LNAPL is observed in wells.
	NSZD	NSZD plays a central role in long-term stability of LNAPL bodies. Therefore, the confirmation of NSZD represents a line of evidence of LNAPL stability.
Mobility	LNAPL age (time since release)	The longer the LNAPL has been in the ground, the less likely it is that a significant mobile fraction exists.
	LNAPL saturations compared to residual levels	Saturations significantly exceeding residual levels indicate a significant mobile fraction.
	LNAPL transmissivity	LNAPL transmissivity exceeding accepted *de minimis* levels may indicate a mobility concern. ITRC (2018) recommends 0.08 m^2/day (0.8 ft^2/day) is a practical limit below which most of the LNAPL can be assumed to exist as immobile residual.
	Recovery system performance	Declining or poor recovery system performance provides an indication that the LNAPL is unlikely to be mobile in the absence of the system-applied gradients. Decline curve analysis and semi-log cumulative recovery plots can be used to estimate the remaining recoverable volume and associated additional operational time needed (see Appendix D).

Parameter	Potential lines of evidence	Notes
Mobility (continued)	LNAPL stability lines of evidence	If an LNAPL body is shown to be stable, it is unlikely that a significant degree of potential mobility remains. Recall that most stable LNAPL bodies will contain some mobile LNAPL that will not contribute to migration/instability. All LNAPL mobility lines of evidence should be considered along with LNAPL stability lines of evidence to assess level of concern.
Recoverability	LNAPL transmissivity	Exceedances of *de minimis* LNAPL transmissivity criterion indicate LNAPL is sufficiently mobile to be considered recoverable. Consider on a plume-scale to assess overall LNAPL body recoverability. LNAPL recovery is considered technically impracticable such that it will not provide a benefit where LNAPL transmissivity is largely *de minimis*.
	Recovery system performance	Recovery tests or operating systems that perform poorly provide evidence of poor recoverability.
	Other LNAPL mobility lines of evidence	Other lines of evidence relating to LNAPL mobility correlate directly with the potential hydraulic recoverability of an LNAPL body

APPENDIX D.

Example graphical analysis of LNAPL recovery system performance

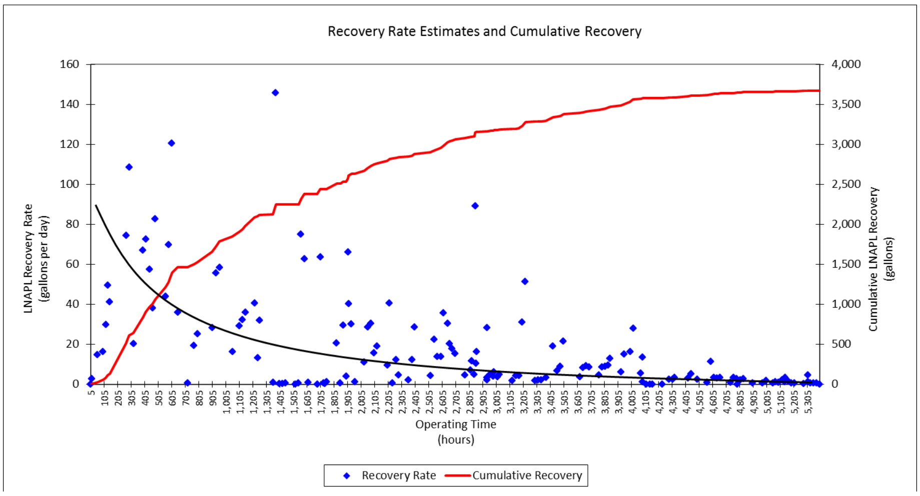


Figure D.1: Sample cumulative and recovery rate plots for an LNAPL recovery system demonstrating an asymptotic recovery rate trend. This system is well past the point of diminishing returns.

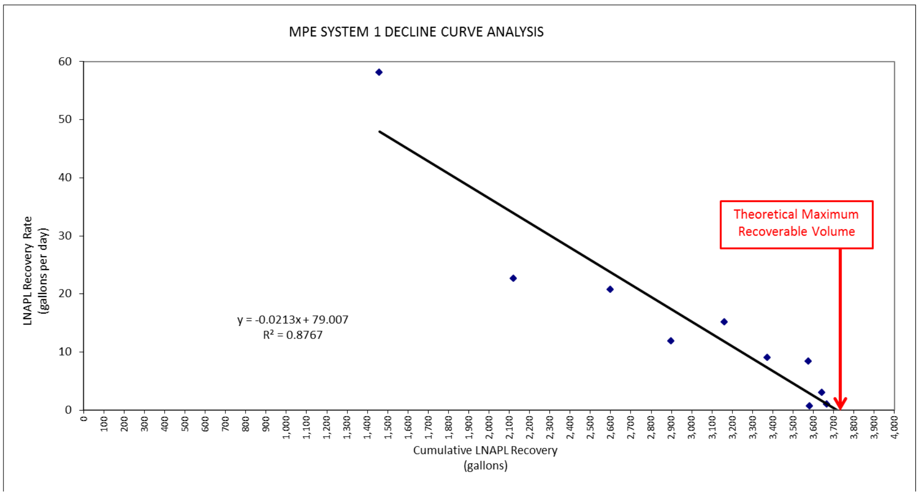


Figure D.2: The latter portion of the decline curve will exhibit a declining trend. The x-intercept of the best fit line through this portion of the curve projects the theoretical limit to a given system's performance. It is noted that the achievement of the theoretical recovery limit may not be cost-effective or provide a net environmental benefit.

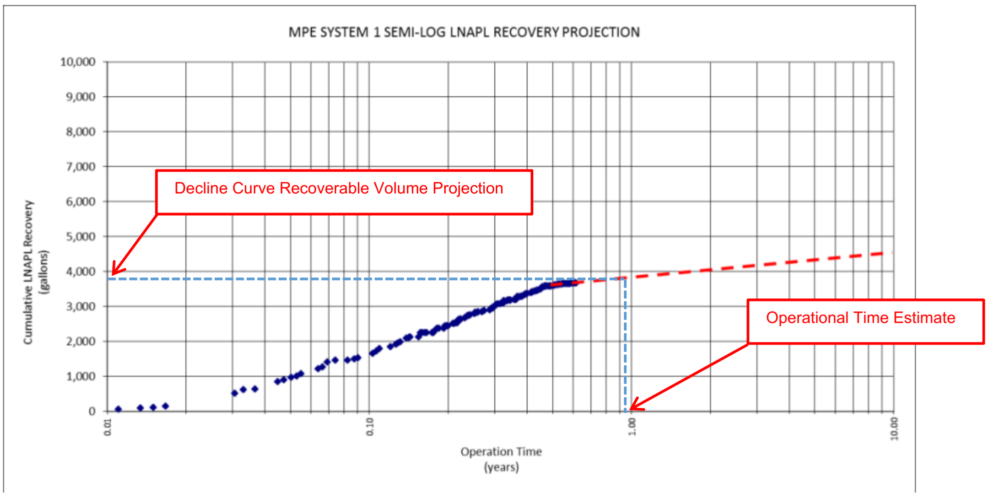


Figure D.3: The decline curve projection can be used with a semi-log cumulative recovery plot to estimate the theoretical remaining operational time for a given system.

APPENDIX E.

Case studies

Case study 1. Gasoline range condensate in a calcareous limestone (Australia)

Site context[9]

The 28 ha site is a sparsely vegetated coastal environment, with a low-elevation. Its surface soils and aquifers are comprised of limestone or lime-cemented dune sand. Aeolian sand dunes overlie limestone in parts of the site. Solution features are evident in places both above and below the water table. The climate is arid subtropical (high humidity summer, warm winter) with an annual average rainfall of about 280 mm. Groundwater is 4 to 14 m below surface and water table fluctuations may be up to 1.5 m driven primarily by tidal forcing and seasonal rainfall recharge. The layout of site boreholes and monitoring locations, and the inferred plume distribution as of April 2018 is shown in Figure E1.

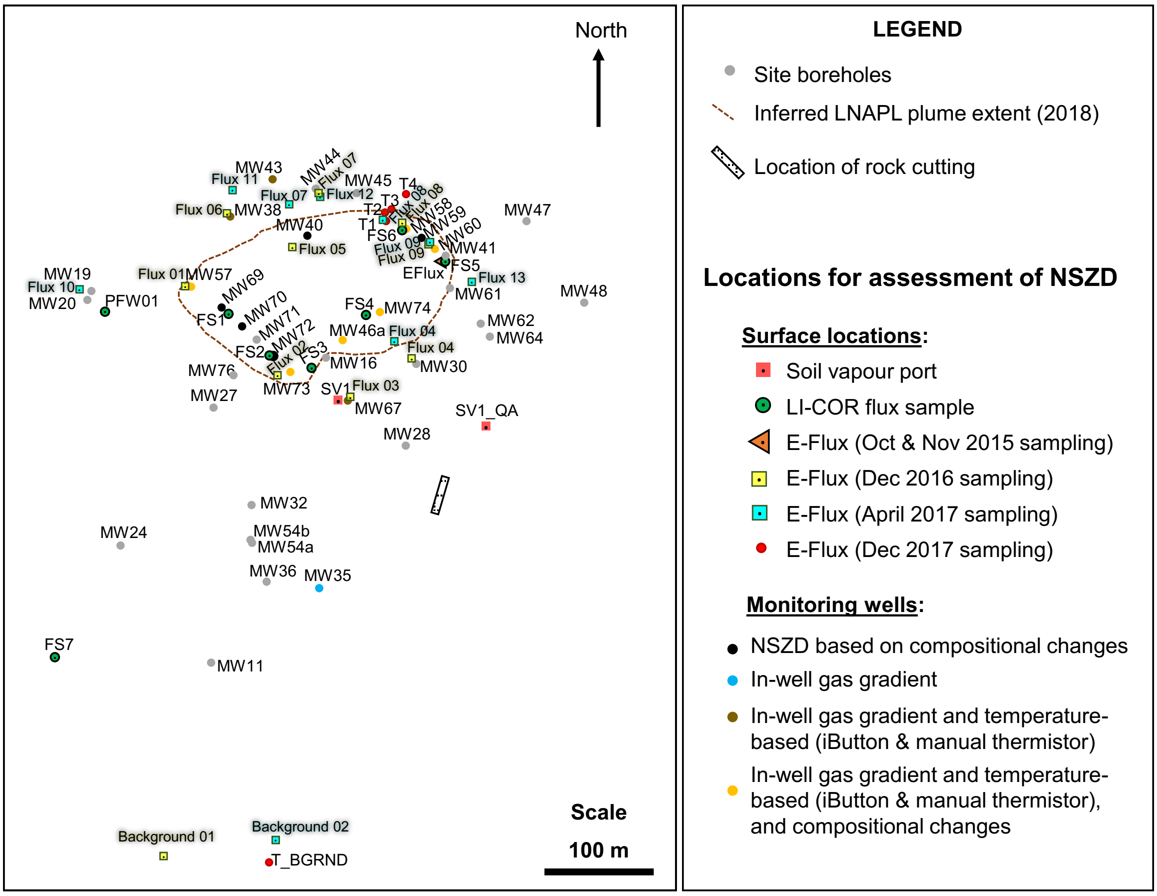


Figure E1: Generalised map of sampling and monitoring locations, and inferred extent of the gas condensate LNAPL plume as of April 2018.

[9] *Case study provided by Rayner et al 2020*

LNAPL in the subsurface resulted from a release of gas condensate from a buried pipeline which was identified in January 2014 with an estimated aerial extent of 4.6 ha. The gas condensate contained C4-C26 carbon range hydrocarbons dominated by the C6-C10 carbon range components. It also contained a high relative abundance of aromatic compounds (including, alkylbenzenes and alkylnaphthalenes) with toluene, methylcyclohexane and *m*/*p*-xylene the highest concentration components by weight. The initial condensate subsurface volume loss was estimated to be 2,830 kL +/- 1,600 kL (or approximately 2,230 tonnes +/- 1,260 tonnes). This was calculated from mass loss estimates from LNAPL compositional changes over time (see later comments on LNAPL fingerprinting) and reconciling this with volume estimates based on in-well product thicknesses, secondary porosity estimates and the areal extent of the LNAPL plume. The range of volume estimates is large due to assumptions in the method stemming from the range of a representative secondary porosity values which are the main subsurface feature where the LNAPL is residing within the fractured limestone. This method of LNAPL volume estimation also assumes equilibrium between the in-well LNAPL and formation, and the degree to which this assumption is satisfied has not been determined at this stage.

Volumes of LNAPL resident in the subsurface during the 2016-18 period, indicate volumes may have reduced by approximately half (refer to Figure E2). If average values of thickness and secondary porosity are applied, then volumes may have decreased from ~1,300 kL to ~600 kL over a 3-year period.

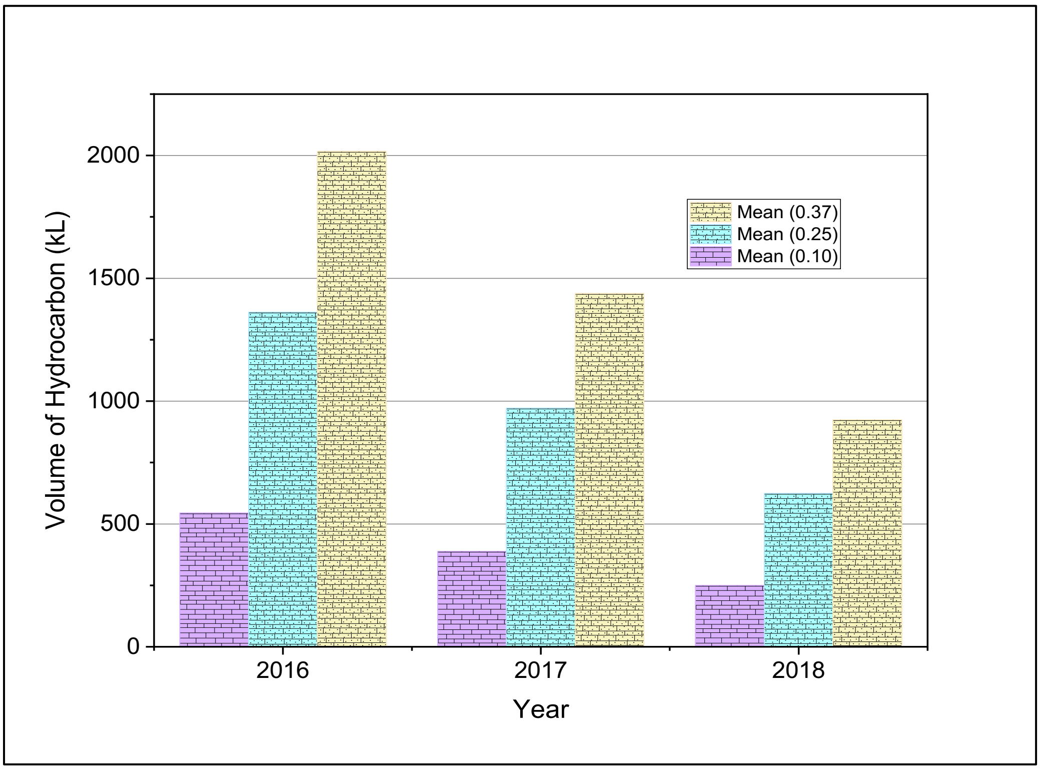


Figure E2: Estimated volume of LNAPL across the site based on the mean LNAPL thickness in wells for years 2016, 2017 and 2018. Three different secondary porosity values are presented.

Active recovery efforts

Recovery techniques including skimming, total fluids pumping and multiphase extraction had an average rate of recovery of 5 L/d, 18 L/d and 17 L/d respectively, from April 2015 to September 2018. During this period, a total of 6,806 L was recovered over a total period of 1,185 days. Some of the recovery was limited by operational infrastructure impeding access to the entire extent of the subsurface LNAPL plume as well as prohibitively high in well vapour concentrations. Active recovery employing 3 methods over the last 3 years has achieved on average c. 5.7 L/d (~1.7 tonnes/yr) LNAPL removal.

NSZD rate estimates

A range of methods were used at the site to provide estimates of NSZD rates. These included ground surface carbon dioxide fluxes (using multi-period and location E-flux and LI-COR), temperature profiling (using iButton strings and via thermistors manually advanced down open wells), soil gases (sampled at the fluid interface from open wells and from multi-depth gas sampling ports), and from LNAPL compositional changes. A tabulation of the ranges of rates for each method are given in Table E1.

Table E1. NSZD rates across methods used, and spatially-weighted mass losses per time.

NSZD methods	**Intrinsic rate estimates** (L LNAPL ha^{-1} yr^{-1})*	**Rate mass/time** (t/yr) (weighted to the plume area)**
Soil surface CO_2 flux	• E-flux: 160 – 34,000 • LI-COR: 1,700 – 12,000	23
Temperature	• iButton strings: 0 - 3,300 • Manual thermistors: 200 – 4,500	4.8
Gas sampling (in well)	• O_2: 34 – 8,900 • CO_2: 27 – 9,000	15
Gas sampling (gas vapour port data)	• O_2: 11,000 – 35,000 • CO_2: 10,000 – 36,000	34 to 110
LNAPL compositional changes	• 35,000 to 87,000 • Based on between 26 and 64% mass loss since release	110 to 280

All rates are background corrected. E-flux flux was determined across three years. Assumed an LNAPL density of 703 kg/m^3 (as octane). Vapour port data is for one location – but different depth intervals;

* *Rates have been determined across a number of locations (except for the vapour port), the range denotes variability across different locations at the site. Values are rounded to 2 significant figures. For the vapour port data the range is estimated by different assumed depth interval concentration gradients; ** A polygon areal weighting approach has been adopted to determine these rates, with the polygon areas scaled to the LNAPL plume area at the site (4.6 ha).*

NSZD rates from temperature profiles were the lowest intrinsic rates and therefore the lowest total mass depletion rates of 4.8 t/yr. Mostly, NSZD rates determined through short term measurement approaches conducted over minutes to days (including: temperature, in-well major gases, CO_2 surface fluxes from LI-COR and E-flux traps) gave lower rates of mass loss, compared to the longer timescale method of LNAPL compositional changes by 10 times or even higher if top of the range estimates are used (i.e. 110 to 280 t/yr). In contrast, major gases from soil vapour ports yielded the highest NSZD rate estimates apart from LNAPL compositional changes due to better depth delineation of major gas concentrations indicating the oxic/anoxic interface.

Dissolution from the LNAPL into groundwater is considered a strong pathway for mass loss (i.e. NSZD) given the high solubility and high relative abundance of aromatic components in the condensate, and hence a pathway for biodegradation within groundwater. The very high rates estimated from LNAPL compositional changes may be due to depletion of the more volatile and water-soluble components in the LNAPL and potentially significant groundwater attenuation via sulfate reduction. Groundwater has marine signatures where LNAPL is not present, and yet sulfate is largely depleted over the entire LNAPL plume area. This large mass removal would be expressed in LNAPL compositional changes but may not be readily reflected in vadose zone gases or temperatures nor in surface flux measurements. It may be a site where groundwater natural attenuation rates have rivalled estimates of vadose zone NSZD rates. Ongoing LNAPL mass removal due to sulfate reduction would depend on a continuing input of sulfate and the availability of hydrocarbon components more easily degraded by this process. No estimates due to sulfate reduction have been made at this stage.

Comparison of active recovery and NSZD rates

The active recovery of LNAPL on site (1.7 t/y) is lower than the estimated NSZD rates by between ~5 and ~50 times for temperature methods and vapour port gas compositions respectively. It is noted that active recovery was restricted by operational infrastructure limiting access to the entire extent of the subsurface LNAPL plume.

At this site, it appears mass loss processes which do not fall under active recovery or vadose zone NSZD measurement techniques, have accounted for perhaps 2 orders of magnitude more LNAPL removal than what has been quantified in the methods being compared in this case study. These losses are associated with dissolution into groundwater, volatilisation into the vadose zone, and subsequent biodegradation processes. These are the subject of further investigation.

It is recognised that the depletion rate of all these processes will change over time as both the removal of more biodegradable and lower molecular weight components through partitioning processes occurs. Thus, while it is recognised that these processes have occurred based on the LNAPL compositional changes it is unlikely that the contribution of these processes to mass loss can be retrospectively quantified without additional fate and transport modelling.

Case study 2. Diesel and crude oil in a sandy aquifer (Australia)

Site context[10]

The site is a large coastal site with multiple LNAPL sources released over long periods of time. In general, the product is highly weathered. The annual average rainfall is approximately 650 mm and the relatively permeable sands allow for relatively rapid downward infiltration of water, subsurface migration of hydrocarbons, as well as the exchange of soil and atmospheric gases. The soil profile and surficial aquifer consists of a sequence of aeolian and littoral calcareous sands. Sometimes thin carbonate-cemented layers are encountered in the vadose zone. Often creamy-tan-coloured sands extended to 2 to 3 m below ground, where a change to grey-coloured sand might occur down to the depth of the bottom of the sand sequence. The sands typically have low organic matter content (i.e. fraction of organic carbon less than 0.03%). In-well LNAPL thickness is controlled by water table elevation which varies seasonally with strongly winter dominant rainfall.

Two primary locations are reported, referred to as locations D6 (diesel) and D10 (crude oil). A background location was used to determine the natural soil (non-LNAPL) NSZD rates to enable the separation of LNAPL degradation from natural soil processes. The aerial extent of recoverable in-well LNAPL was determined from contoured in-well LNAPL thicknesses of ≥ 50mm for 2018. For diesel the monthly areal extent of mobile LNAPL varied from 1.4 to 3.8 ha, however there was no measurable evidence ≥ 50mm of LNAPL thickness in the crude area wells for 2018. The nominal area for NSZD was based on mapping of the 2004 product type distributions determined from in-well LNAPL samples by a combination of density, viscosity and whole oil analysis. The 2004 areal extent of the diesel plume was determined to be 28 ha, and the crude oil plume 6.0 ha. These areas were used to extrapolate NSZD annual mass losses from rate estimates in 2018 as they represent areas where LNAPL was historically present and is still likely to be present as immobile LNAPL, i.e. as entrapped and residual LNAPL.

[10] *Case study provided by Rayner et al 2020*

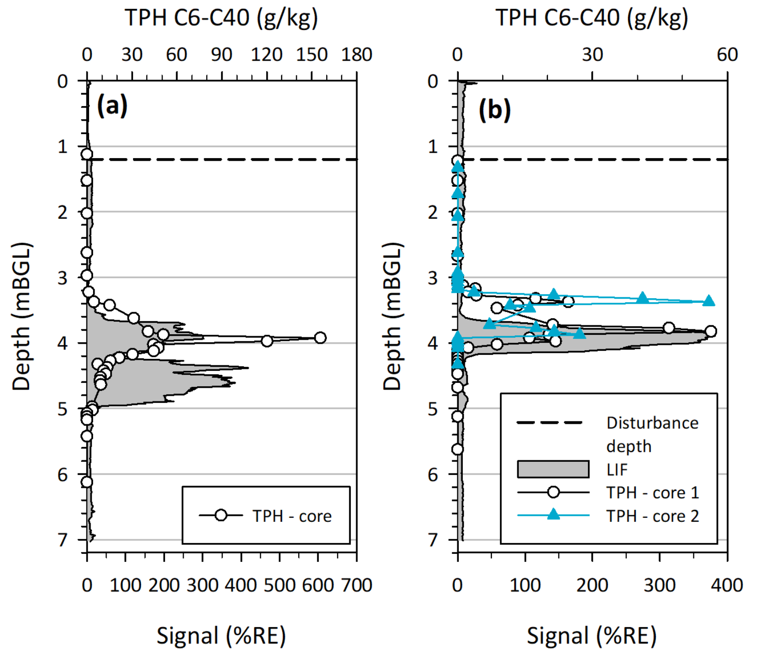


Figure E3: Laser induced fluorescence (LIF) depth profiles, along with LNAPL TPH determined from soil cores for site D6 (diesel location) (a) and D10 (b) (crude oil location).

The water table was ~ 4.6 m below ground level (BGL) at location D6 and was ~3.6 mBGL at D10.

Over a 16-year period in-well LNAPL thicknesses varied seasonally and over time from 0 m to close to 1 m, with decreasing trends over this time period. Figure E3 shows Laser Induced Fluorescence (LIF) depth profiles, along with TPH determined from soil cores for site D6 and D10 (cores from two locations <20 m apart). Both profiles show a discrete smeared distribution of LNAPL over perhaps 1.5 m for the diesel site and perhaps 1 m for the crude site. LNAPL C6-C40 TPH concentrations in the soil cores are about 2–3 times higher at the diesel site.

Active recovery efforts

Figure E4 shows the total LNAPL mass removed by active recovery spanning the years 1985 to 2018 from all recovery operations on site. The annual mass recovery ranges from a maximum of 3600 t in 1988 to a minimum of 21 t in 2018. In general, there has been a substantial reduction in mass recovery over 3 decades, with occasional spikes due to new releases (for example 2004). In 2018 the 21 t recovered comprised of c. 17.5 t coming from diesel impacted areas, with no recovery from the crude oil areas due to limited recoverable LNAPL, with no measurable in-well thickness ≥ 50mm.

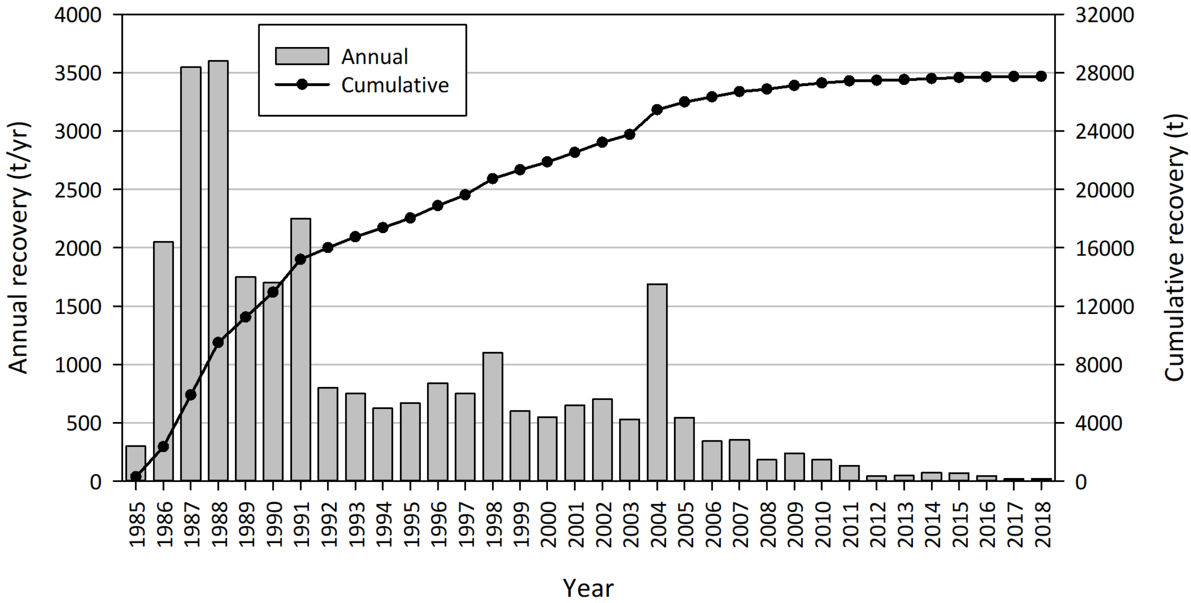


Figure E4: Annual mass recovery from the whole site from 1985 to 2018.

NSZD estimates

A range of methods were used at the diesel and crude locations to estimate NSZD rates. Three thermistor strings were buried within 20 m of each other at each of the two locations. Additionally, a central multi-level gas sampling installation and piezometers were emplaced at both the D6, D10 and background locations. Oxygen, carbon dioxide and other major gases were sampled and analysed from the multilevel sampler to determine a depth profile, and at the same time major gases were sampled in the open piezometer from 0.3 m above the LNAPL interface. Both were used to calculate rates. Triplicate LI-COR CO_2 surface fluxes were determined at three locations within a 2 to 5 m radius of the central installations. NSZD estimates were averaged across all measurements. Tables E2 and E3 provide NSZD rate estimates for each method at each location.

***Ta*ble E2. Tabulation of NSZD rates across methods used at D6 (diesel), and spatially-weighted mass losses per time.**

NSZD methods	**Intrinsic rate estimates** (L LNAPL ha^{-1} yr^{-1})*	**Rate mass/time** (t/yr) (assuming areal extent)**
Soil surface CO_2 flux	• LI-COR: 6,000	• 120
Temperature	• Buried thermistors: 6,000 to 8,800	• 120 to 170
Gas sampling (in well)	• O_2: 13,000 • CO_2: 14,000	• 250 • 270
Gas sampling (gas vapour port data)	• O_2: 10,000 • CO_2: 12,000	• 190 • 230

*All rates are background corrected. The LI-COR are averages across three replicates at three locations within 2-5 m of the central gas sampling locations. NSZD temperature ranges are from three thermistor strings; * Values are rounded to 2 significant figures; ** Assumed an LNAPL density of 703 kg/m^3 (as octane), and areal extent of diesel LNAPL (28 ha) from the 2004 distribution determined by a combination of LNAPL density, viscosity and whole oil analysis (by gas chromatography).*

Table E3. Tabulation of NSZD rates across methods used at D10 (crude oil), and spatially-weighted mass losses per time.

NSZD methods	Intrinsic rate estimates (L LNAPL ha^{-1} yr^{-1})*	Rate mass/time (t/yr) (assuming areal extent)**
Soil surface CO_2 flux	• LI-COR: 5,800	• 24
Temperature	• Buried thermistors: 1,000 to 3,000	• 4 to 13
Gas sampling (in well)	• O_2: 6,800 • CO_2: 7,500	• 29 • 32
Gas sampling (gas vapour port data)	• O_2: 15,000 • CO_2: 17,000	• 63 • 71

*All rates are background corrected. The LI-COR are averages across three replicates at three locations within 2-5 m of the central gas sampling locations. NSZD temperature ranges are from three thermistor strings; * Values are rounded to 2 significant figures; ** Assumed an LNAPL density of 703 kg/m^3 (as octane), and areal extent of crude oil LNAPL (6.0 ha) from the 2004 distribution determined by a combination of LNAPL density, viscosity and whole oil analysis (by gas chromatography).*

To convert intrinsic LNAPL NSZD rate estimates (L LNAPL ha^{-1} yr^{-1}) to mass removal rates (t/yr) for each location, the 2004 areal extent of the diesel plume of 28 ha and the crude oil plume of 6.0 ha were used. We note that total mass removal rates may be reduced if soil gas movement is inhibited – as it might occur below concreted or asphalt areas within the 28 and 6 ha areas; or if soils have high moisture contents. Inhibiting oxygen ingress reduces NSZD biodegradation rates.

For the diesel location, the highest NSZD rates were estimated by major gas analysis. The oxygen and carbon dioxide in-well and depth profile multilevel data provide similar rates of 10,000–14,000 L LNAPL ha^{-1} yr^{-1} (or 190 to 270 t/y). Surface flux and temperature estimates were comparable to each other in the range 6,000–8,800 L LNAPL ha^{-1} $yr^{-1}$and (or 120 to 170 t/y).

For the crude oil location, intrinsic NSZD rates were highest when estimated by major gas analysis. However, in contrast to the diesel location, the oxygen and carbon dioxide depth profile multilevel data at the crude oil location provided 2–3 times higher NSZD rate estimates of 15,000–17,000 L LNAPL ha^{-1} yr^{-1} (or 63 to 71 t/y) compared to the in-well major gas method. The temperature method yielded the lowest NSZD rates of 1,000–3,000 L LNAPL ha^{-1} yr^{-1} (or 4 to 13 t/y). Surface flux and in-well gas sampling methods yielded comparable estimates.

NSZD rate estimates from temperature data were consistent across multiple thermistor strings and measurement times. Rate estimates for the diesel location were 3 to 4 times higher compared to the crude oil location.

Comparison of active recovery and NSZD rates

Active LNAPL recovery from the D6 (diesel) location was approximately 17.5 t in 2018. NSZD mass loss is of the order of 120 to 270 t/y across the estimated extent of the diesel LNAPL plume.

At the D10 (crude oil) location, there was no active LNAPL recovery due to limited recoverable LNAPL, with no measurable in-well thickness ≥ 50mm. There is a large range of calculated LNAPL mass removal across all NSZD methods of 4 to 71 t/y representing the crude oil plume, largely due to low rates derived from temperature gradient methods. If temperature estimates are excluded, crude oil NSZD mass estimates were in the narrower range of 24 to 71 t/y.

Overall diesel NSZD rates are 7 to 15 times higher than the maximum LNAPL liquid diesel recovery rates in 2018. For crude oil a direct comparison could not be made in 2018 due to there being no crude oil available for removal via active recovery. Therefore, mass losses associated with crude oil were solely as a result of NSZD. Across all methods, NSZD rates for diesel were comparable to those for crude oil, with differences between methods of up to a factor of 2 (excluding temperature). Research into the variability between NSZD methods caused by compositional, spatial and temporal conditions is the subject of ongoing investigations at this field site.

Case study 3. Diesel and gasoline in a fractured sedimentary rock strata (Australia)

Site context[11]

The site is predominately flat and approximately 30% of the 3.2 ha area is covered with concrete or bitumen. The subsurface strata typically consists of 1 m of clay, overlying weathered phyllite (metamorphosed siltstone) over the next 3 m depth. Beneath this is a fractured phyllite. The primary permeability is thought to be low. The water table has been measured as between 3 m to a maximum of 14 m below ground surface, with significant inferred groundwater gradient across the site as indicated in Figure E5. Groundwater velocities of about 20 m/y have been estimated. Joint and fault system fractures appear to influence groundwater flows. Dissolved plumes have remained stable.

Extensive investigations have been carried out at the site (Figure E5) and both MPE and NSZD rates have been determined. LNAPL on site is designated as motor spirit and diesel – recent analysis suggests primary LNAPL in wells is weathered winter diesel (*n*-alkanes depleted or removed); and occurrences of weathered gasoline. The subsurface LNAPL area is estimated to be approximately 1 ha.

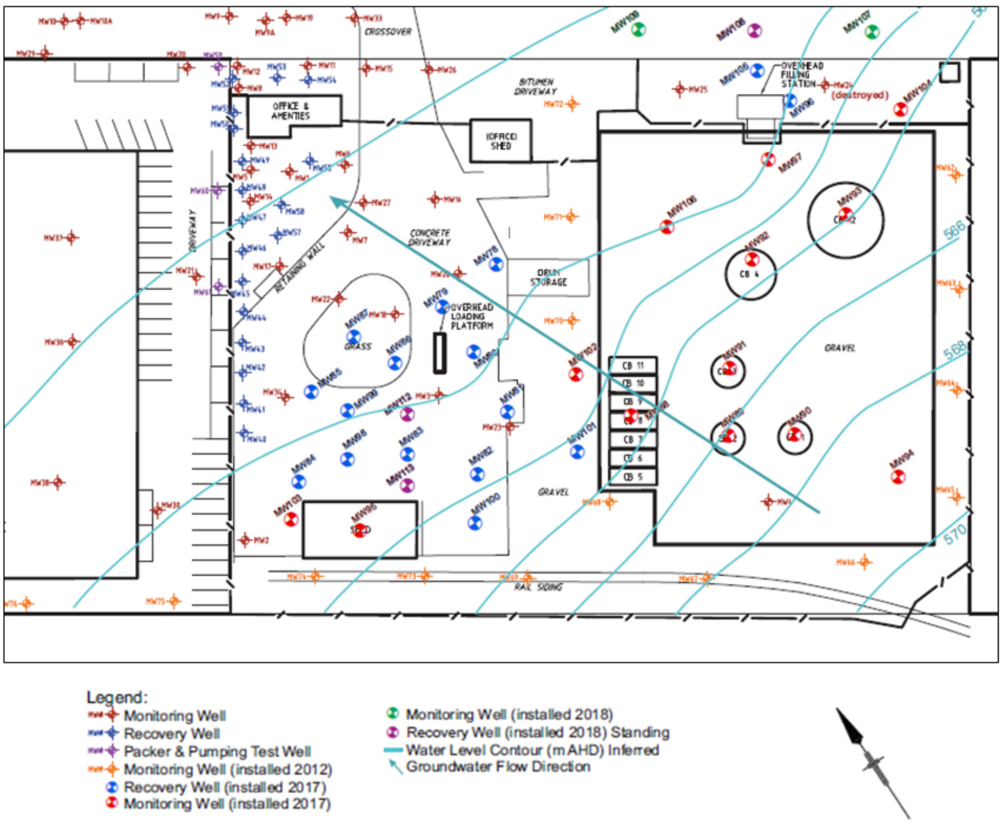


Figure E5: Layout of some of the monitoring and recovery wells on site G, along with groundwater contours and key site features.

[11] *Case study provided by Rayner et al 2020*

Active recovery efforts

MPE was applied at the site over the period 2012-2018 from up to 37 well locations. A significant volume of LNAPL has been recovered over this period (up to 77,500 kg) with the majority in 2013, and a total of ~25,500 kg since 2015 (Table E4). LNAPL mass recovery has largely halved each year up to 2018 (Table E4), disproportionally to reduced run times. Proportional to run times, recovery rates have dropped from 3.8 kg/hr in 2015 to less than 1.0 kg/hr in 2018. Whilst seemingly successful, MPE data indicates that more than 99% of hydrocarbon removed has been through the vapour phase; and measurement of vapour emissions are typically the most problematic to do accurately as a metric of MPE mass removal performance. Despite extensive MPE application, LNAPL still resides in wells local to LNAPL recovery areas, presumably due to the lack of interconnection between some areas across the site.

Table E4. Mass of LNAPL removed (kg hexane equivalent) by MPE

LNAPL recovery	2015	2016	2017	2018	Total for 2015 2018
LNAPL mass removed (kg hexane)	13,817	6,748	3,209	1,682	25,456
Run hours	3,614	4,058	2,759	1,774	12,205
LNAPL mass kg/hr	3.8	1.7	1.2	0.94	2.1

NSZD estimates

Two methods were used at the site to provide estimates of NSZD rates – in well temperature profiling and in-well soil gases. NSZD rates are tabulated in Table E5. Temperature profiling was undertaken by lowering a string of thermistors set at regular depth intervals down existing wells on site and measuring temperature following a 1-hour equilibration time. This was undertaken at 24 locations across the site. Four background locations were measured – and estimates presented here are after subtracting the highest temperature background location from others, and then averaging across the twenty non-background locations. One non-background location gave the same or lower rates as the background location (i.e. effectively a zero-degradation rate estimate compared to background).

The gradient method was used to determine NSZD rates from in-well and atmospheric oxygen and carbon dioxide concentrations. Oxygen and carbon dioxide concentrations were determined by sampling gas from 300 mm above the LNAPL or water interface in existing wells on site using both an in-situ gas meter and laboratory (gas chromatography) analysis. Very good correlation was observed for both oxygen and carbon dioxide between the in-situ and laboratory analysed samples. The gas diffusion coefficient and thermal conductivity values were based on literature values for comparable lithologies and indicative soil moisture contents taken from previous laboratory analysis of materials during coring and drilling activities. Values represent averages across nearly 40 measurements, with some repeated sampling from the same well.

Table E5. Tabulation of NSZD rates across methods used, and spatially-weighted mass losses per time.

NSZD methods	Intrinsic rate estimates (L LNAPL ha^{-1} yr^{-1})*	Rate mass/time (kg/yr) (assuming areal extent)**
Temperature	• Manual thermistors: 0 – 8,800 (Average = 3,500)	• 0 - 6,200 (Average = 2,500)
Gas sampling (in well)	• O_2: 0 - 1,700 (Average = 620) • CO_2: 0 - 740 (Average = 300)	• 0 - 1,200 (Average = 440) • 0 - 520 (Average = 210)

*All rates are background corrected. Soil gas total porosity and air-filled porosity were assumed to be 0.45 and 0.2 respectively. Higher air-filled porosity gives higher rates; * Values are rounded to 2 significant figures; ** Assumed an LNAPL density of 703 kg/m^3 (as octane), and area of LNAPL is estimated to be 1 ha.*

NSZD rates determined from in well gas sampling are quite low. NSZD rates based on oxygen were much higher on average (and for the maximum of the range) than carbon dioxide NSZD rates. The reason for this is not clear. The magnitude of the rates determined from the gas data are strongly dependent on the total porosity and air-filled porosity estimates.

Average NSZD rates determined from the temperature profiles were 5 times greater than the average determined from the oxygen gradient, and approximately 10 times greater for average NSZD rate calculated from carbon dioxide data.

The cause of the different rate estimates requires further investigation.

Comparison of active recovery and NSZD rates

The most recent LNAPL recovery rate in 2018 is about 1.7 t/yr. On average the major gas NSZD rates vary from 0.210 to 0.440 t/y (4 to 8 times lower than MPE recovery) with a maximum based on oxygen of 1.2 t/y (1.5 times lower than MPE recovery rates). For temperature, on average NSZD rates are 2.5 t/y which is 1.5 times greater than the 2018 recovery rate, and 3.6 times the 2018 LNAPL recovery rate for the maximum NSZD rate determined from the temperate data. Longer term data sets are being collected to confirm these findings.

Case study 4. Jet fuel in sand (Australia)

Site context[12]

The site has been an active fuel terminal since 1929. The site LNAPL resulted from a diesel release in 2007 and a jet fuel release in 2014. The LNAPL migrated offsite and currently is found both onsite and below a neighbouring industrial building. Investigation history includes well gauging, soil/groundwater sampling, and indoor air testing in neighbouring building (Figure E6). Remedial efforts have been implemented since 2014 including continuous skimming and periodic events with a mobile MPE system operating in both MPE and SVE modes. The application of the MPE system included the installation of a vapour cap to minimise the short-circuiting of induced vacuum. NSZD was evaluated to serve as a baseline indicator of LNAPL degradation rates and to support an eventual active remediation endpoint demonstration.

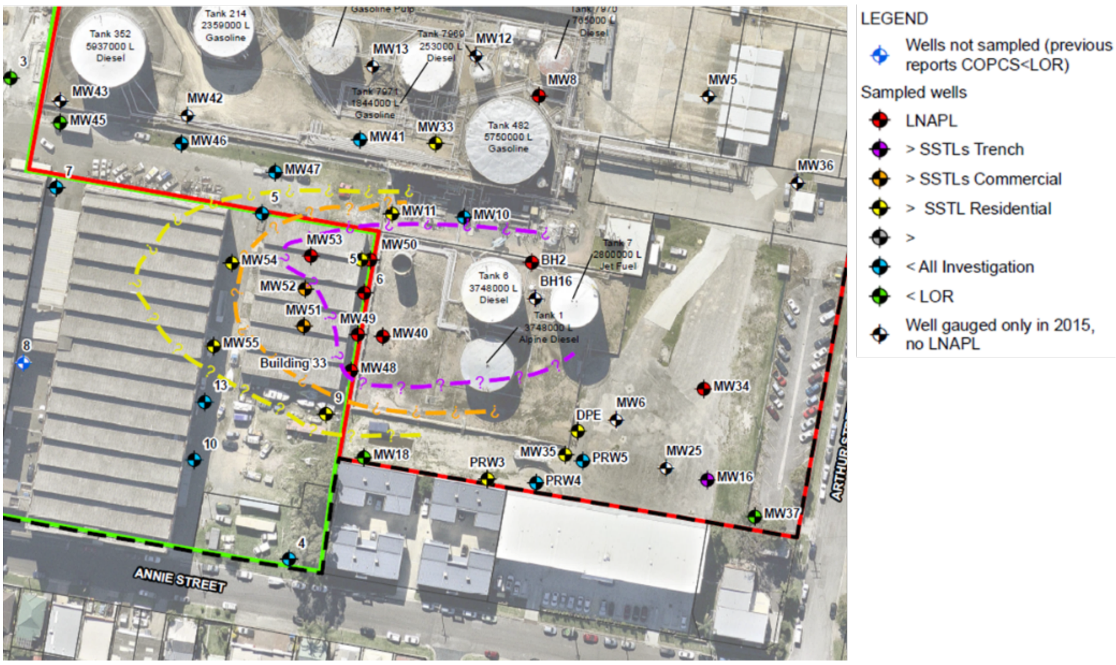


Figure E6: Site plan showing representative results of well gauging and sampling.

NSZD monitoring

A single baseline event was performed via the CO_2 efflux methods in two steps. An initial screening level step was performed in a grid pattern in accessible portions of the site using a dynamic closed chamber (LI-COR Biosciences 8100A) to evaluate near surface CO_2 anomalies and compare with other site data relating to contaminant distribution. The second step involved the use of CO_2 Traps at a smaller number of locations to provide results that were integrated over a longer time period and included a more conclusive built-in correction for background CO_2 (using ^{14}C unstable isotope analysis) that is not resulting from LNAPL degradation.

The results of the two steps are shown in Figures E7 and E8, respectively, along with Table E6. It is noted that the results of Step 1 matched well spatially with other site data on LNAPL presence/extent. This site therefore represents an example of where

[12] *Case study provided by GHD*

NSZD screening could be used as a rapid, non-intrusive technique for LNAPL body delineation. In this case, the distance between NSZD monitoring points was approximately 10 metres and measured rates were assumed to apply to a radius of influence of 5 metres from the point of measurement in order to convert NSZD units of volume per unit area per unit time to units of volume per unit time for direct comparison to LNAPL recovery system performance.

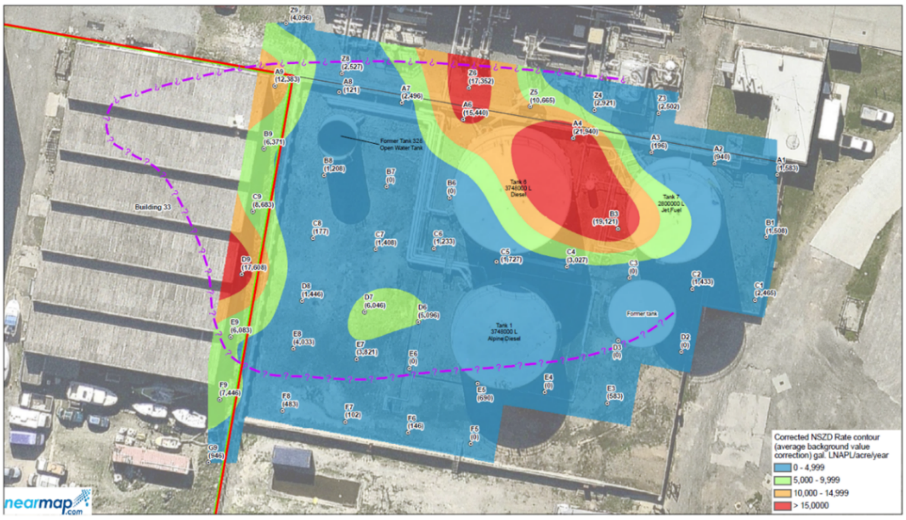


Figure E7: Dynamic closed chamber NSZD rate estimates and contours.

Figure E8: CO_2 trap NSZD rate estimates.

Table E6. Summary of NSZD rate estimates.

Location	Flux chamber NSZD rate estimate (L LNAPL ha^{-1} yr^{-1})	CO_2 trap NSZD rate estimate (L LNAPL ha^{-1} yr^{-1})
A6	144,000	145,000
A9	116,000	125,000
B3	179,000	21,000
B7	0	10,000
D7	56,000	9,000
D9	164,000	73,000

LCSM summary

LCSM component	Notes
NSZD	NSZD confirmed to be active at significant rates. The presence of methane emanating through floor cracks in neighbouring building provides an additional indication of NSZD activity.
LNAPL mobility/ recoverability	Lack of widespread observations of LNAPL in wells and results of LNAPL recovery efforts suggest that the LNAPL is not significantly mobile or recoverable. A comparison of LNAPL recovery performance against different projections of long-term NSZD rates based on single event results showed that a conservative assumption of even 10% of measured rates would outperform actual LNAPL recovery (Figure E9).
LNAPL body/ dissolved phase stability	Monitoring since 2014 indicates LNAPL body and dissolved plume stability.
Potential exposures	While the detection of methane entering the neighbouring building through floor cracks represents a positive, direct indication of LNAPL degradation, in this case it also represents a potential vapour intrusion risk. Figure E10 provides an example of indoor (floor crack) methane monitoring results over time. Methane concentrations have been detected above the lower action criterion of 500 ppm but have not approached the upper action limit of 12,500 ppm. Therefore, this remains a potential exposure as the source-pathway-receptor linkage is currently incomplete. The primary exposure pathway identified for the LNAPL contamination is direct exposure for construction and intrusive maintenance workers, which is being managed by the implementation of an institutional/administrative control (environmental management plan).

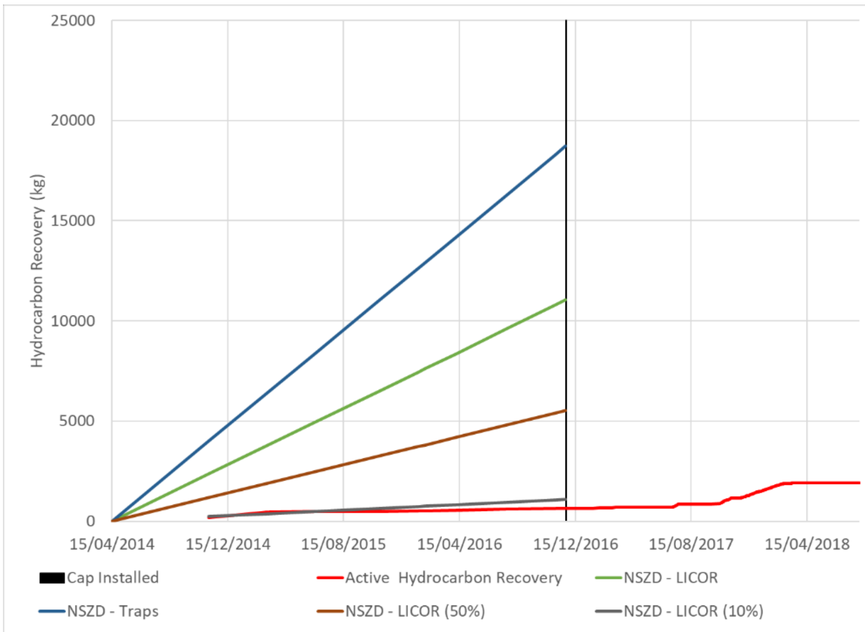


Figure E9: Comparison of different NSZD rate projections with actual LNAPL recovery performance (skimming and MPE combined).

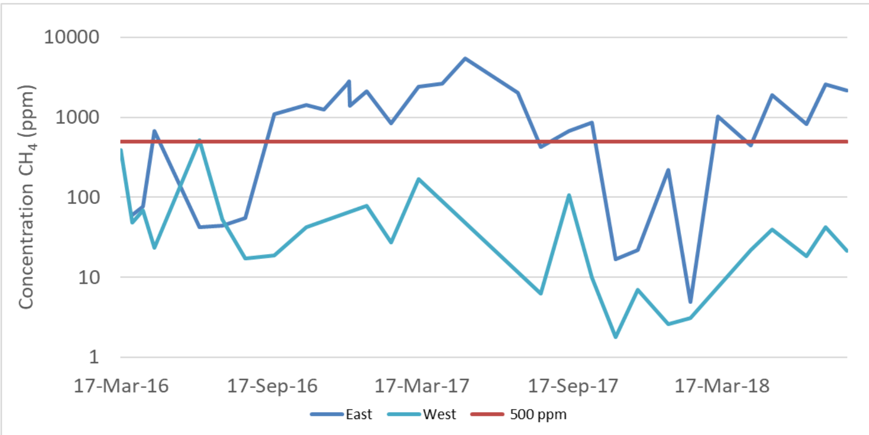


Figure E10: Sample indoor (floor crack) methane monitoring results.

Management objectives

Potential management objectives	Critical considerations	Result
Saturation-based	Stability: monitoring history indicates stable LNAPL body. Recoverability: Well gauging history, historical recovery performance, NSZD rates indicate there is not a need for or net benefit to be gained through ongoing LNAPL recovery for saturation reduction.	No saturation-based objectives applicable.
Compositional	Methane intrusion into neighbouring building.	Compositional objective exists to mitigate methane intrusion.

Management strategy

In this case, the fact that NSZD likely significantly exceeds LNAPL recovery performance is superseded by the potential risk associated with the methane intrusion and the related compositional objective. The application of MPE continues in order recover methane, vapour-phase LNAPL and/or to induce airflow beneath the neighbouring building to oxidise the methane.

It is anticipated that MPE will continue until methane concentrations can be consistently demonstrated to be below the lower action criterion, which will represent a practical end-point to MPE operation given the lack of saturation-based objectives, the fact that NSZD is already likely to be significantly outperforming LNAPL recovery, and the fact that the primary exposure pathway (direct contact) is effectively controlled. At that point, NSZD monitoring will be utilised to justify transitioning to NSZD as the long-term LNAPL management strategy. The need for controls as a long-term risk management component will be contemplated at that time.

Monitoring

Long-term monitoring needs will be addressed once the active remedial stage transitions to NSZD.

Case study 5. Petrol/diesel in weathered/fractured rhyodacite (Australia)

Site context[13]

The site is an active fuel depot with both documented (1991) and suspected undocumented fuel releases, with various site investigation activities completed starting in 1991. The fractured bedrock setting exhibits a complex fracture network that has been mapped and a single major discontinuity appears to control groundwater flow and LNAPL body geometry (Figures E11–E13). It was hypothesised that this discontinuity would also serve as the preferential pathway for soil gas migration, which would constitute a 25-metre offset between the discontinuity's intersection of the water table and its projection to surface. No active remedial trials have been undertaken at the site. NSZD was evaluated as a potential primary LNAPL management component.

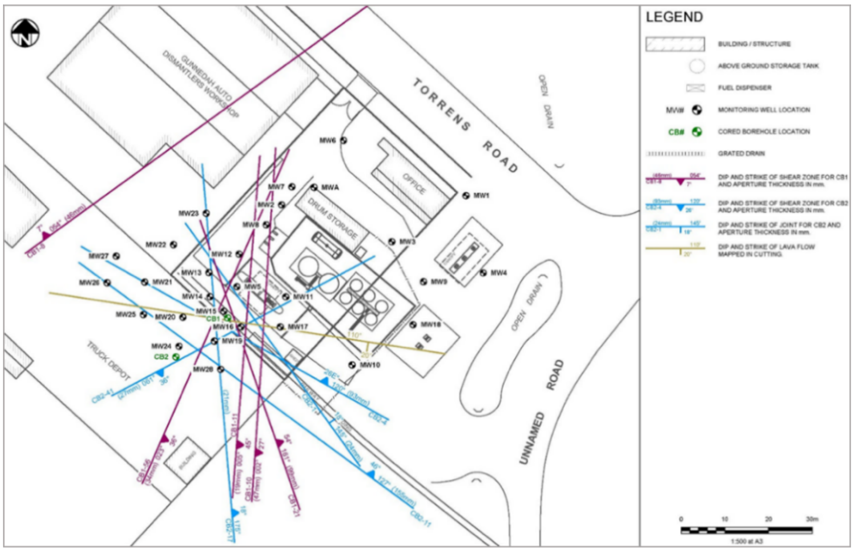
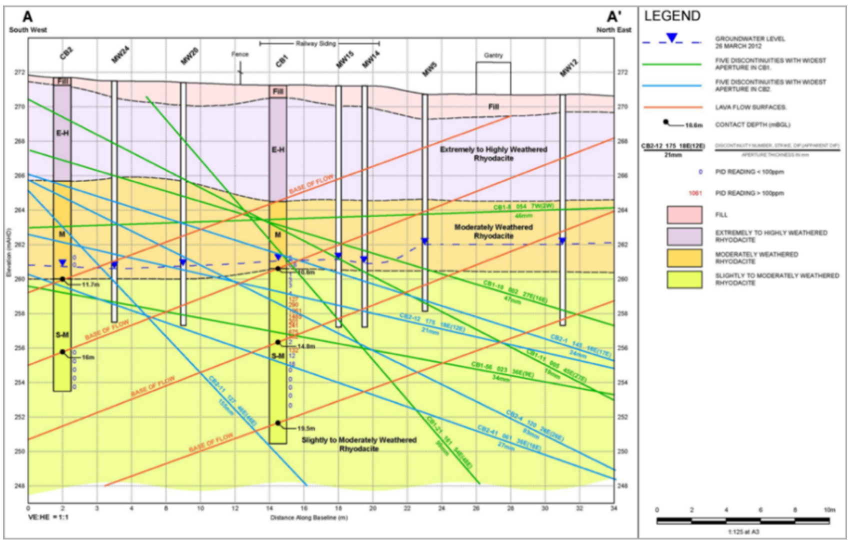


Figure E11: Site plan with plan view of major discontinuities.



[13] *Case study provided by GHD*

Figure E12: Cross-sectional view of major discontinuities. CB2-41 was identified as the controlling feature based on LNAPL and groundwater plume geometry.

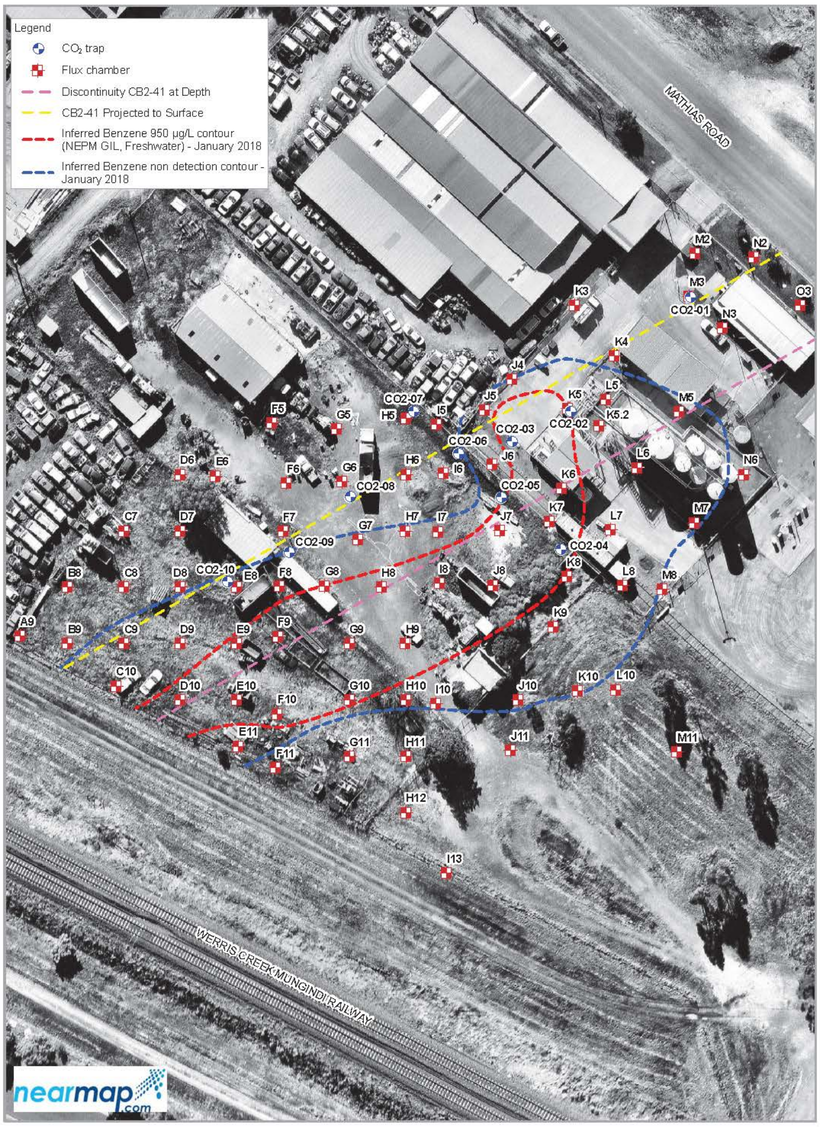


Figure E13: Site plan showing dissolved plume alignment with Discontinuity CB-41.

NSZD monitoring

NSZD monitoring consisted of a multi-step approach involving CO_2 efflux and biogenic heat methods. An initial round of a small number of readings was obtained with a dynamic closed chamber (LI-COR Biosciences 8100A) to test the soil gas migration pathway hypothesis. The results seemed to match the hypothesis, and a subsequent round of dynamic closed chamber testing was completed site-wide, the results of which are illustrated in Figure E14. The second step involved the use of CO_2 Traps at a smaller number of locations to provide results that were integrated over a longer time period and included a more conclusive built-in correction for background CO_2 that is not resulting from LNAPL degradation (using ^{14}C unstable isotope analysis). Concurrently, vadose zone temperature profiles were obtained in order to estimate NSZD rates via the biogenic heat method for comparison with the CO_2 efflux methods. All NSZD assessment locations are shown in Figure E13.

The CO_2 flux testing results are presented in Figure E14. The DCC results were initially viewed as a screening level assessment due to the complexity of background correction from highly variable levels of vegetation at surface (i.e. variable levels of background CO_2 sources). A sampling of the complexity in surface cover is provided in Figure E15.

Figure E14: NSZD estimates based on DCC (left) and CO_2 Trap (right) results

Figure E15: Variability in vegetative surface cover illustrates complexity in background correction of DCC data in real-time.

Vadose zone temperature profiling was performed using a temperature-equipped water level meter, which proved to have too long a stabilisation time associated with it to produce results that were considered consistently reliable (i.e. too much uncertainty as to whether apparently stable readings were actually stable). However, certain profiles were deemed to be useable given the shape of the profiles and the magnitude of apparent temperature anomalies relative to their location (Figure E16).

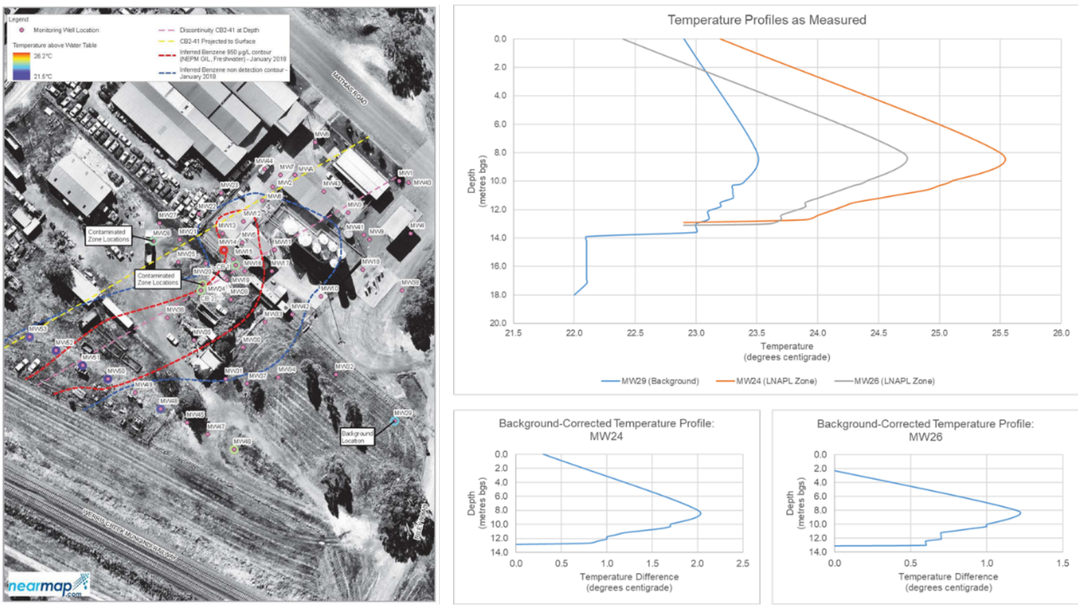


Figure E16: Subsurface temperature monitoring results.

The resulting maximum NSZD estimates compared by method are shown in Table E7.

Table E7. Summary of maximum NSZD rate estimates by method

DCC	CO_2 traps	Biogenic heat
20,000 L LNAPL ha^{-1} yr^{-1}	15,000 L LNAPL ha^{-1} yr^{-1}	12,000 L LNAPL ha^{-1} yr^{-1}

LCSM Summary

LCSM component	Notes
NSZD	NSZD confirmed to be active at rates that are consistent with what is commonly observed at LNAPL sites.
LNAPL mobility/ recoverability	Lack of widespread observations of LNAPL in wells and stability of LNAPL body and dissolved phase indicate that LNAPL body is likely to be mostly present at residual levels.
LNAPL body/ dissolved phase stability	Monitoring history indicates LNAPL body and dissolved plume stability.
Potential exposures	No potential exposures associated with LNAPL in-place. Vapour risk assessment confirmed current land use could continue both onsite and offsite with no exposure concerns.

Management objectives

Potential management objectives	Critical considerations	Result
Saturation-based	Stability: monitoring history indicates stable LNAPL body. Recoverability: Lack of widespread observations of LNAPL in wells indicates a small potentially recoverable fraction.	No saturation-based objectives applicable.
Compositional	No unacceptable exposures identified associated with LNAPL in place.	No applicable compositional objectives.

Management strategy

NSZD has been proposed as the primary component of the LNAPL management strategy given that:

- There is no expected benefit to the implementation of active engineered techniques based on the LCSM.
- There are no applicable saturation-based or compositional remedial objectives.

The proposed strategy has gained preliminary regulatory acceptance with formal comment to come.

Monitoring

It is anticipated that long-term monitoring will be required as part of the overall management strategy to confirm the LCSM conclusions regarding the stability of impacts.

Case study 6. Diesel in interbedded clay and sand (USA)

Site context[14]

The site is an operating railyard with historical releases of diesel fuel. Active LNAPL recovery (skimming) has been performed since 2003. Initially, LNAPL recovery was implemented at six wells in the immediate vicinity of the release. The system was expanded to add ten additional extraction wells within the LNAPL extent surrounding the original six extraction wells (Figure E17).

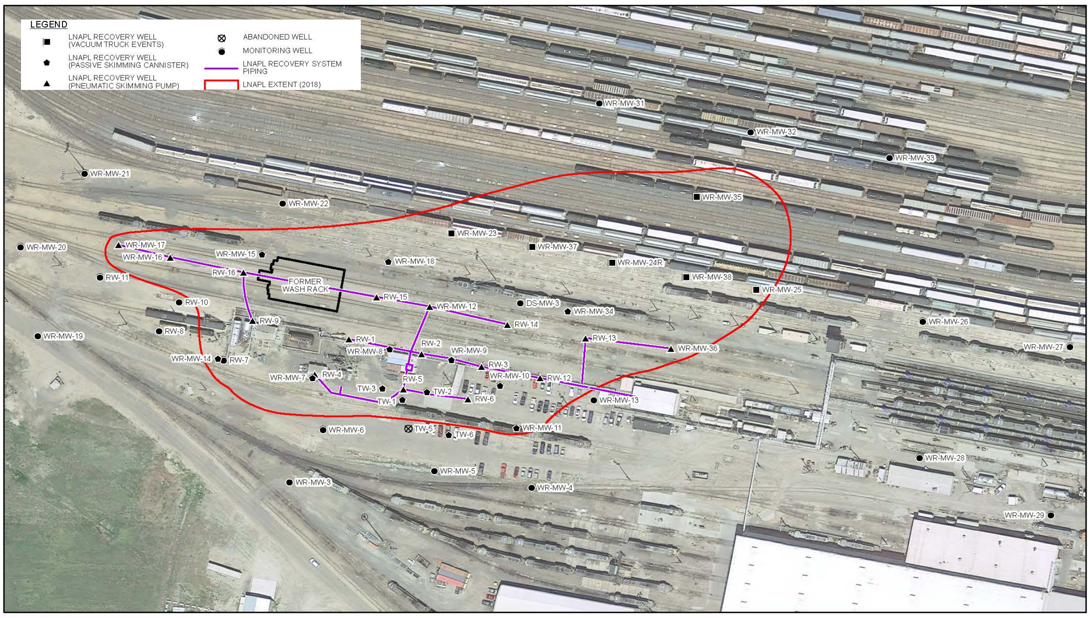


Figure E17: Site plan showing LNAPL body extent and LNAPL recovery system layout.

System LNAPL recovery rate performance followed an asymptotic trend over time. Notably, the expansion of the system from six to sixteen wells did not result in a measurable increase in recovery performance. As such, there was no tangible benefit realised to the expansion of the system outside the immediate area of the release. Figure E18 provides a graphical representation of system performance over time. A newer release is observable in the increased recovery rates more recently. These increased recovery rates declined such that they approached pre-release levels after approximately 1 year.

A quantitative LNAPL mobility/recoverability evaluation was performed that included re-characterisation of the site using laser-induced fluorescence and soil core petrophysical testing to quantify LNAPL saturations and the volumetric fraction that might be recoverable. Subsequently, LNAPL transmissivity testing was performed to provide an additional line of evidence supporting the endpoint to LNAPL recovery and/or to focus the ongoing application of LNAPL recovery where it would provide value (dependent on results). Soil core test results indicated that a significant recoverable fraction was not present (i.e. LNAPL saturations were at residual levels). In

[14] *Case study provided by GHD*

addition, LNAPL transmissivity results indicated recoverable LNAPL was only present in the immediate release area (Figure E19), which was consistent with the observation that the expansion of the LNAPL recovery system outside this area provided no added benefit.

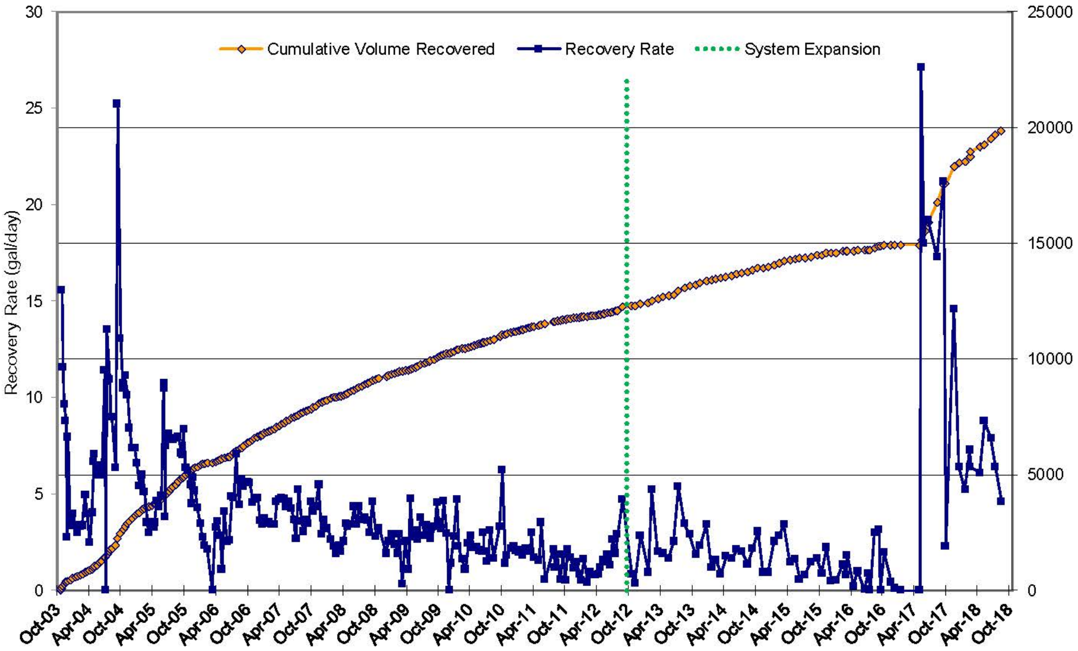


Figure E18: Active LNAPL recovery performance history.

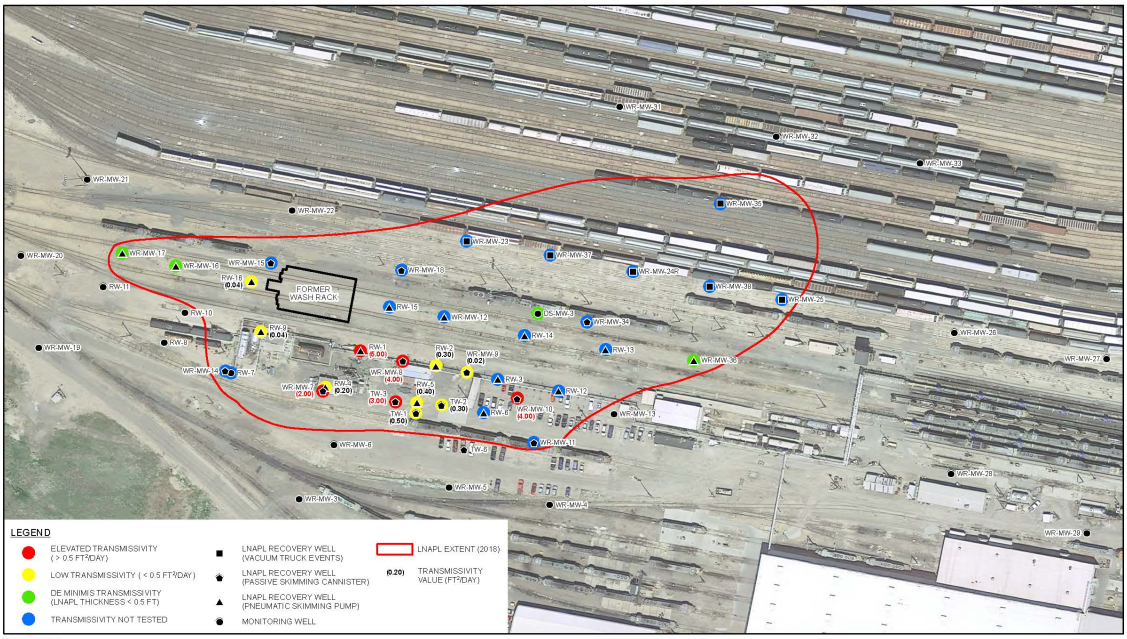


Figure E19: Site plan showing LNAPL body extent and LNAPL transmissivity results.

There were no unacceptable exposure scenarios associated with the LNAPL in place. There were no receptors for the vapour intrusion pathway and dissolved petroleum hydrocarbons were non-detect immediately outside the LNAPL body extent. In addition to the LNAPL mobility/recoverability lines of evidence, years of monitoring of the dissolved phase extent and the area where LNAPL was observed in wells indicated both were stable.

NSZD monitoring was completed in order to evaluate the net benefit of ongoing LNAPL recovery (i.e. support a demonstration of a practical endpoint to LNAPL recovery), and to support the long-term management of the residual LNAPL in place

NSZD monitoring

A single NSZD monitoring event was performed via the CO_2 efflux methods in two steps. An initial screening level step was performed in an approximate grid pattern in accessible portions of the site using a dynamic closed chamber (LI-COR Biosciences 8100A) to evaluate near surface CO_2 anomalies and compare with other site data relating to contaminant distribution. The second step involved the use of CO_2 traps at a smaller number of locations to provide results that were integrated over a longer time period and included a more conclusive built-in correction for background CO_2 (using ^{14}C unstable isotope analysis) that is not resulting from LNAPL degradation.

The results of the two steps are shown in Figures E20 and E21, respectively. In order to develop a spatially-weighted average NSZD rate based on the dynamic closed chamber results, the Thiessen Polygons method was utilised (Figure E20). Since the CO_2 Trap results were obtained from an approximate transect of the LNAPL body and similarly spaced locations, an arithmetic average of the results was used with the total LNAPL areal extent to convert NSZD rates from area-based units. It is noted that the CO_2 Trap results shown in Figure E21 include an apparently anomalous result that appeared to be biased high. It was not well understood why this result was biased high, but it was hypothesised that stratigraphy could have been producing a chimney effect in the area. In the interest of producing a conservative estimate of potential NSZD rates, this result was omitted from the related averaging.

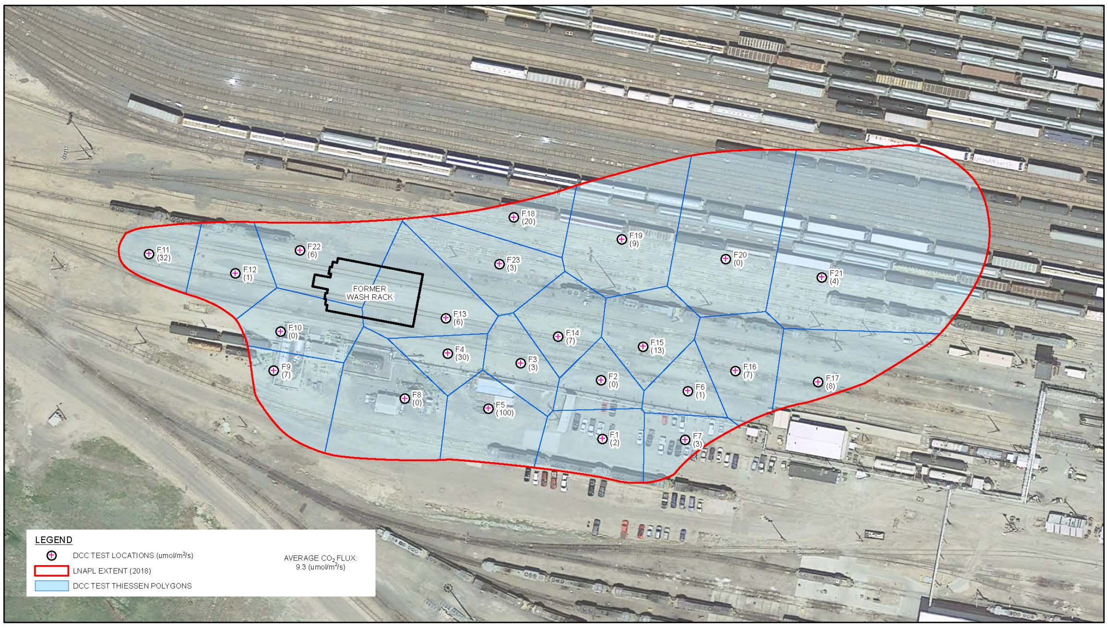


Figure E20: Site plan showing dynamic closed chamber results with Thiessen Polygons.

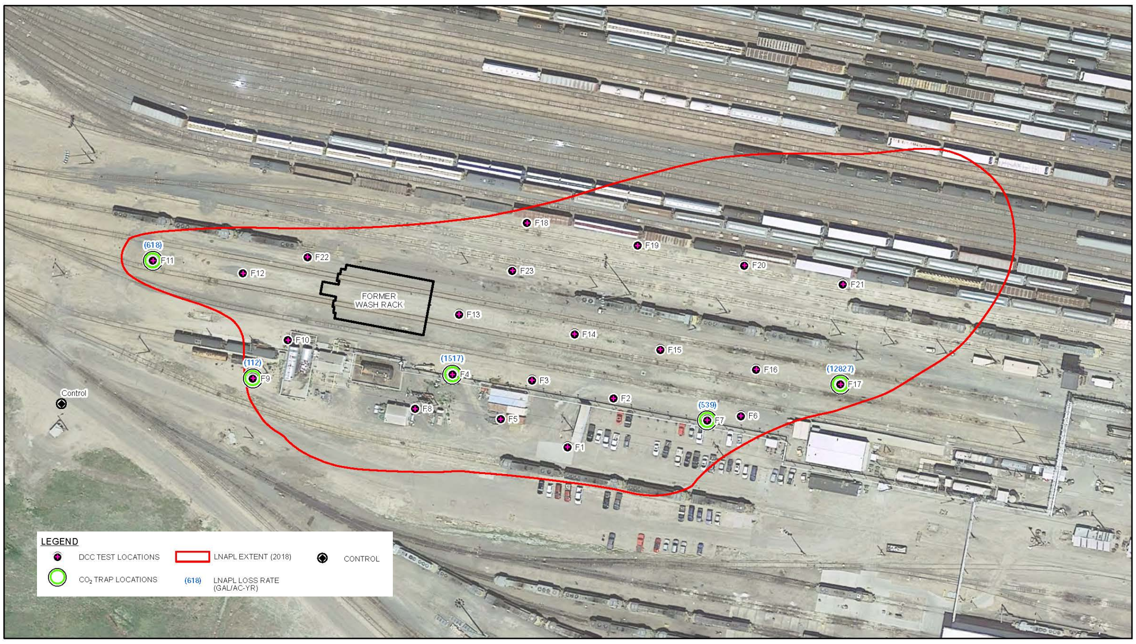


Figure E21: Site plan showing CO_2 trap transect and results.

The maximum NSZD rate estimate from each method is shown in Table E8. The spatially-weighted average NSZD rate estimates are presented and contrasted with the LNAPL recovery performance history in Table E9.

Table E8. Summary of maximum NSZD rate estimates.

Dynamic closed chamber results (L LNAPL ha^{-1} yr^{-1})	CO_2 trap results (L LNAPL ha^{-1} yr^{-1})
187,000	120,000

Table E9. Summary of spatially-weighted average NSZD rate estimates and LNAPL recovery performance.

NSZD rate estimate based on spatially-weighted average of dynamic closed chamber results (L LNAPL yr^{-1})	NSZD rate estimate based on average of CO_2 trap results (L LNAPL yr^{-1})	LNAPL recovery performance history (L LNAPL yr^{-1})
130,000	15,000	2018: 5,000 2017: 13,000

LCSM summary

LCSM component	Notes
NSZD	NSZD confirmed to be active at rates that exceed LNAPL recovery performance.
LNAPL mobility/ recoverability	Multiple lines of evidence indicate the LNAPL is effectively immobile and unrecoverable, with the small fraction of recoverable LNAPL remaining concentrated within the immediate area of the release where LNAPL transmissivities exceed *de minimis* levels.
LNAPL body/ dissolved phase stability	Monitoring history indicates LNAPL body and dissolved plume stability.
Potential exposures	No potential exposures associated with LNAPL in place.

Management objectives

Potential management objectives	Critical considerations	Result
Saturation-based	Stability: monitoring history indicates stable LNAPL body. Recoverability: Multiple lines of evidence indicate that the LNAPL body is largely present as unrecoverable residual, however, an area of elevated LNAPL transmissivity remains in the release area.	No technical saturation-based objectives are applicable. However, a regulatory saturation-based objective exists to recover LNAPL to the maximum extent practicable despite the lack of technical benefit.
Compositional	No unacceptable exposures identified associated with LNAPL in place.	No applicable compositional objectives.

It is noted that, in this case, the respective regulatory framework does not currently consider the net benefit of the activity in the determination of maximum extent practicable.

Management strategy

Based on the LCSM and identified objective of recovering LNAPL to the maximum extent practicable, the following strategy was proposed and has since gained regulatory acceptance:

- Discontinue active LNAPL skimming at ten wells outside the immediate release area based on recovery performance history and LNAPL transmissivity.
- Concentrate ongoing LNAPL recovery activities in release area where LNAPL transmissivity exceeds *de minimis* levels.
- Continue recovery until LNAPL transmissivity is reduced to *de minimis* levels.

It is anticipated that the NSZD monitoring results will be used to support a transition to NSZD as the long-term LNAPL management strategy once the LNAPL transmissivity endpoint has been reached.

Monitoring

Long-term monitoring requirements remain to be determined. It is anticipated minimal monitoring will be required given that the LCSM already includes years of monitoring and multiple lines of evidence indicating the LNAPL body is stable, largely present as residual, and there is no unacceptable exposure.

Case study 7. Gasoline with minor diesel and lube oil in variably weathered basalt

Site context[15]

The source of LNAPL contamination is from a petroleum fuel terminal and the approximate area with wells containing measurable LNAPL is around 2.7 ha (Figure A.1) with a dissolved plume extending beyond this region to the south. The topography slopes gradually to the southeast and a tidal river is located approximately 500 m east of the boxed area shown in Figure E22. The direction of groundwater flow is to the southeast and the depth of groundwater varies between 7 and 10 m below ground. The climate is mild temperate with an average annual rainfall of 550 mm.

The site is underlain by between 2 and 4 m of clay and sandy or silty clay overlying fractured, variably weathered basalt. The physical properties of the basaltic aquifer are highly variable due to the degree of weathering and fracturing within the basalt. Characterisation of the lithology at nearby locations (400 m north) through diamond coring and downhole geophysics indicates zones of higher permeability joint openings and vesicles, with near surface clayey horizons and weathered zones and denser basalt deeper in the profile that may act as aquitards. There may be periodic perching of water associated with the upper clayey horizons. The hydraulic parameters are likely to be highly variable, depending on the development of secondary porosity. The regional hydraulic properties of the basalt aquifer are hydraulic conductivity (0.18–35 m day^{-1}), transmissivity (40–170 m^2 day^{-1}) and porosity 1–5%.

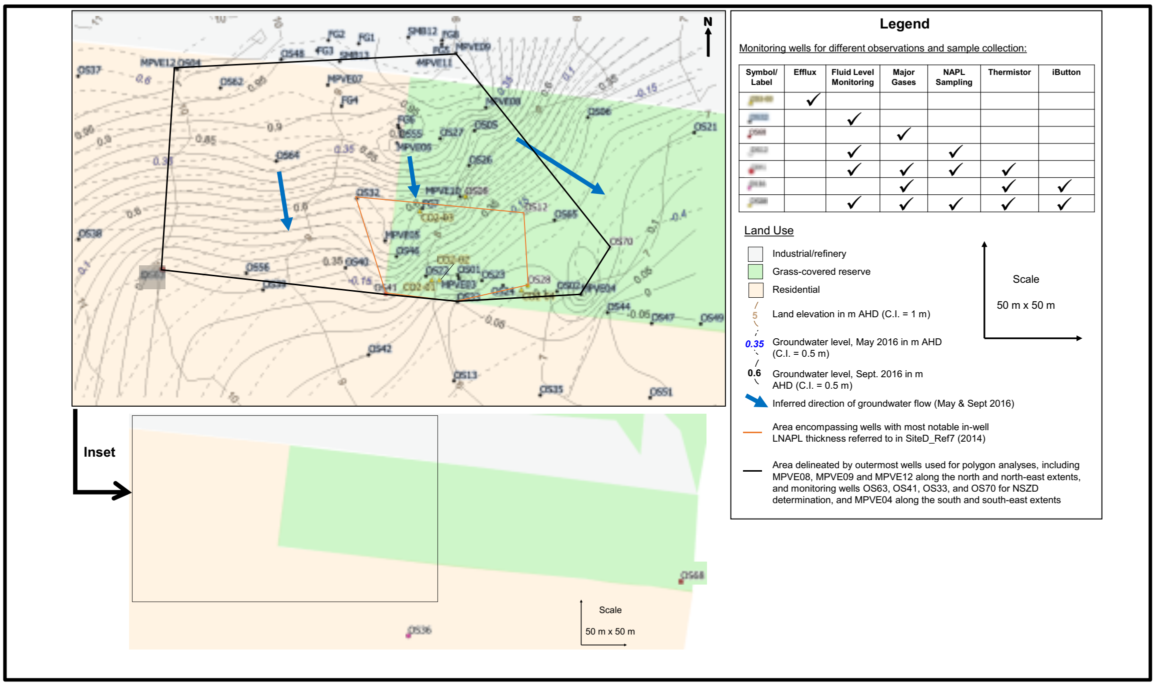


Figure E22: Generalised map of sampling and monitoring locations.

LNAPL contamination is due to leakage from storage tanks and pipelines and/or surface spills over several decades. The petroleum in the subsurface contains a

[15] *Case study provided by Rayner et al 2020*

mixture of different product types including gasoline, kerosene, diesel and lubricant oil range products (C5-C40 carbon range) in various proportions.

Active recovery efforts

Product recovery involved vapour extraction using a multiphase extraction (MPE) system consisting of 12 extraction wells manifolded to a single collection and vapour/liquid waste treatment system. The extraction wells were arranged in three fields of four wells with extraction possible from individual or multiple wells at any time (Figure E23). The daily mass of VOCs (volatile organic compounds) recovered is shown in addition to a green dashed line indicating a daily target of 23 kg (Figure E24). The daily target equates to 8.4 t/yr which was is close to the estimated total recovery for the last 12 months of operation (8.7 t). It is noticeable that during the last 12 months of operation, the rate of recovery was progressively declining: 32 kg/d (11.7 t/yr) for the first 6 months, 16 kg/d (5.8 t/yr) for the second 6 months.

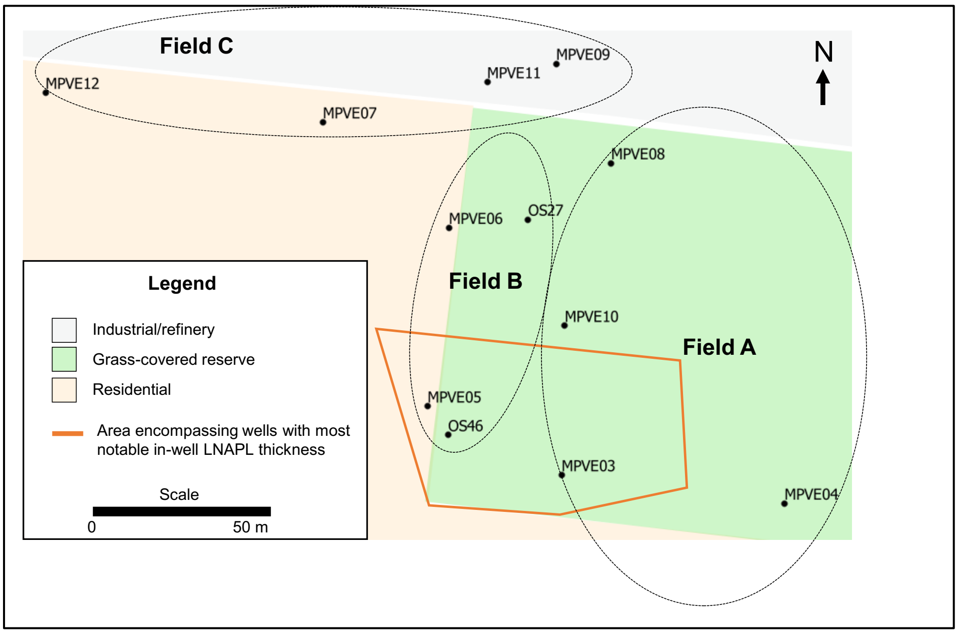


Figure E23: Groups of four extraction wells per field for MPE conducted between June 2013 and July 2015.

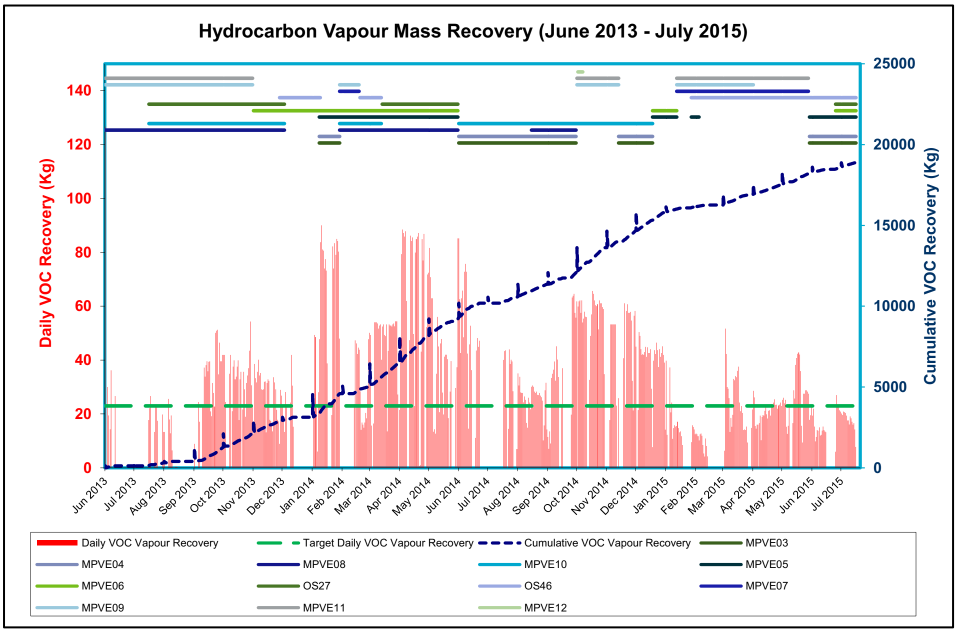


Figure E24: Daily and cumulative VOC vapour recovery for MPE applied to 12 extraction wells.

NSZD rate estimates

A range of methods were used at the site to provide estimates of NSZD rates. These included ground surface carbon dioxide fluxes (E-flux), temperature profiling (using iButton strings and thermistors manually placed in existing wells), and soil gas (O_2 sampled 300 mm above the fluid interface from existing wells). A summary of the range of rates determined for each method are given in Table E10.

Table E10: NSZD rates estimated by different methods, and annual spatially weighted mass loss.

NSZD methods	**Intrinsic rate estimates** (L LNAPL ha^{-1} yr^{-1})*	**Rate mass/time** (t/yr) (weighted to the plume area)**
Soil surface CO_2 flux	• Traps: 0 – 4,400	• 1.9
Temperature:	• iButton strings: 2,065 • Manual thermistors: 2,800 – 5,100	• 3.9 † • 6.9
Gas sampling (in well)	• O_2: 280 – 1,100	• 1.4

*Assumed an LNAPL density of 703 kg/m³ (as octane); * Rates have been determined across a number of locations, the range denotes variability across different locations at the site. Values are rounded to 2 significant figures; ** A polygon areal weighting approach has been adopted to determine these rates, with the polygon areas scaled to the LNAPL plume area at the site (2.7 ha), except where noted (†).*

In-well oxygen data yielded the lowest NSZD rates and an overall NSZD mass depletion of 1.4 t/yr. Temperature profiling gave the highest NSZD rates and overall NSZD mass depletion of 6.9 t/yr across the assumed impacted area at the site. Surface E-flux data was shown to be highly variable across a relatively small area (c. 10 to 20 m apart) which appears partly related to soil moisture conditions at the time of measurement. This is expected due to the relatively fine textured upper layers found at the site.

Relative mass loss estimates based on LNAPL composition changes between 2013 and 2019 were in the order of 1 to 24%.

Comparison of active recovery and NSZD rates

The target daily VOC recovery mass of 23 kg equates to around 8.4 t/yr. Remedial recovery efforts over the last 6 months of operation recovered approximately 5.8 t/yr, when recovery operations ceased. NSZD rates were estimated to be between 1.4 and 6.9 t/yr with the highest rate being from the temperature gradient method using manual thermistor data. These rates overall are comparable, but in general lower than what was being achieved by active recovery. The high variability in rate estimates for the same method at different times, or between methods suggests additional monitoring will establish greater certainty in long term NSZD depletion rates.

Case study 8. Diesel and minor lube oils in fractured, heavily-weathered basalt

Site context[16]

The site is located on a large coastal peninsula with the area containing LNAPL estimated to be around 18 ha. This area includes both mobile and immobile LNAPL (i.e. residual and entrapped LNAPL which may not currently be expressed in monitoring wells but has historically showed evidence of LNAPL in wells). The lithology consists of alluvial deposits and a thin clayey horizon overlying ridges of heavily weathered basalt. The topography varies between about 5 and 13 m AHD and is largely controlled by the underlying ridges of basalt (Figure A.1). The climate is tropical to arid with infrequent, high intensity storms. Within the past decade, the average annual rainfall has been between 100 and 770 mm. The vadose zone contains preferential flow paths such that the water table is highly responsive to storm events. The overall annual variation in the water table is large, i.e. typically around 4 m, and the depth to groundwater is typically between 3 and 16 m below ground.

The best estimate of porosity within the fractured basalt in the area containing LNAPL is around 10% (ranging between 3 and 30%) but depends largely on the extent of weathering and development of secondary porosity as unfractured basalt is likely to have porosity less than 3%. Estimates of hydraulic conductivity vary over three orders of magnitude from 0.001 to 1 m/d. Due to the low transmissivity over much of the aquifer, an increase in the water table elevation following a recharge event, tends to persist over an extended recession period. Mobility of the LNAPL in the aquifer is controlled by variations in the water table, which dictates whether the LNAPL is isolated or connected with conducting fracture systems. The layout of the site boreholes and monitoring locations, and the inferred plume distribution as of October 2017 is shown in Figure E25.

It is estimated approximately 1,000 m^3 of diesel was spilled or leaked into the subsurface at the facility over a period between 1997 and 2000. Product types observed in the LNAPL samples from the site include diesel and lubrication oil range product types.

[16] *Case study provided by Rayner et al 2020*

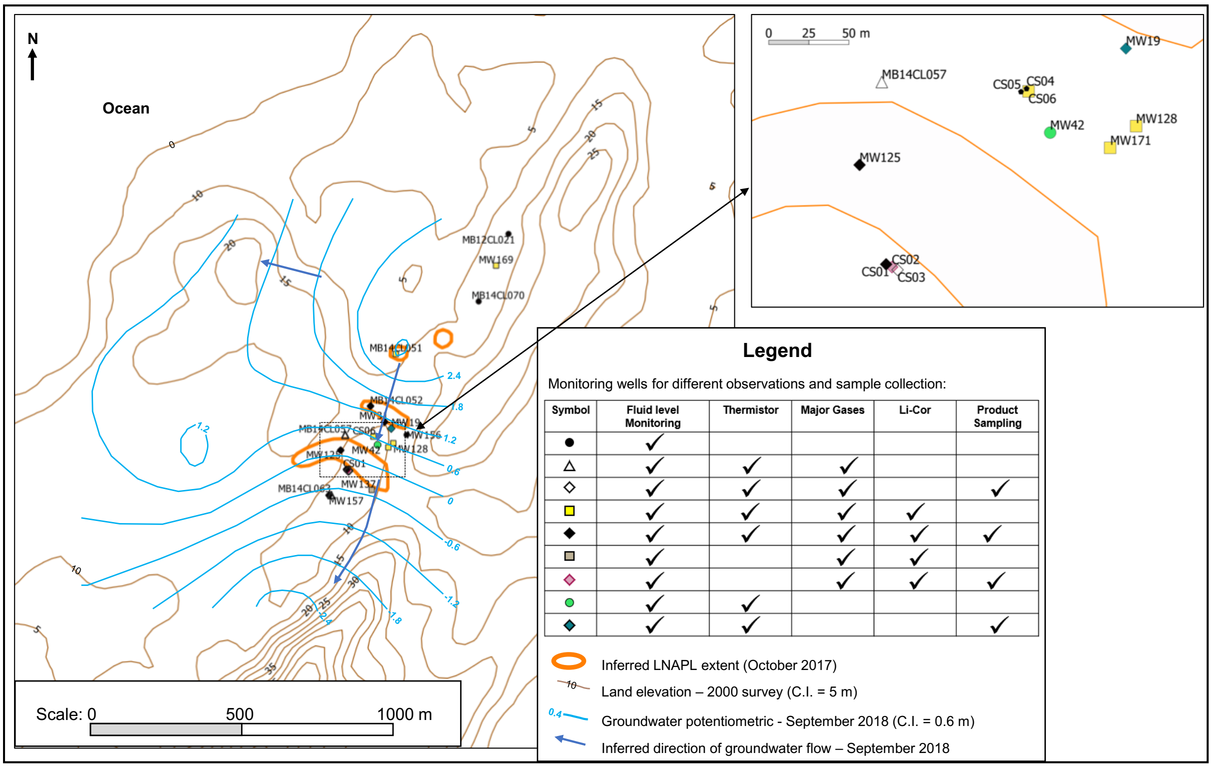


Figure E25: Generalised map of sampling and monitoring locations.

Active recovery efforts

Recovery techniques included skimming and drawdown, total fluids recovery, vacuum enhanced recovery, and multiphase extraction (MPE). Remediation efforts to recover the free phase product commenced in May 1998 with skimming, and approximately 50,000 L of diesel was recovered. Between 2012 and 2013, testing of different active recovery techniques was undertaken by CSIRO as summarised in Table E11.

Recovery rates ranged from 6 to 13 L/d (approximately 1.8–3.8 t/y) with short term (<1 day) LNAPL recovery peaking at 33 L/d. Recovery rates for the duration of these trials were largely controlled by the water table elevation and large amounts of groundwater was associated with the removal of the LNAPL using these techniques. Between the single and dual phase recovery operations in 2012 and the more aggressive technologies in 2013, there was a single torrential rainfall event of 226 mm, resulting in a 3 to 4 m rise in the water table. This resulted in much of the mobile LNAPL becoming immobile as a result of being water occluded within the pores and fractures and largely unrecoverable during the 2013 trials.

Table E11:.LNAPL recovery operations at the site over a three-year period.

Method	Relative water table condition	Average in- well LNAPL thickness (m)	Short term LNAPL recovery rate (L/day)	Long term LNAPL Recovery rate (L/day)	Water made during recovery (L/d)	Comments
Total fluids/skimming and drawdown	Low	0.5	33	6	2000 to 5000	--
VER	0.5 m higher than in 1. above	0.01 to 0.07	9	3.5	2250 to 7300	Comparable LNAPL mass recovery with vapour phase
MPE	As for VER above	0.006		13	430 to 16,600	Less LNAPL recovered in vapour phase

NSZD rate estimates

A range of methods were used at the site to provide estimates of NSZD rates. These included ground surface carbon dioxide fluxes (E-flux and LI-COR) and temperature profiling using iButton and thermistor strings equilibrated in existing monitoring and recovery wells.

A tabulation of the ranges of rates for each method are given in Table E12 and an example of the polygon spatial weighting approach for the thermistor data is presented in Figure E26. Rates for LI-COR were confounded by relatively high rates measured at the background location resulting from vegetation. These results are not presented here as only one location recorded a background corrected rate greater than zero, emphasising the importance of including multiple background locations, particularly at complex sites.

Relative mass losses based on LNAPL compositional changes between 2011 and 2019 were estimated to be between 6 and 21%.

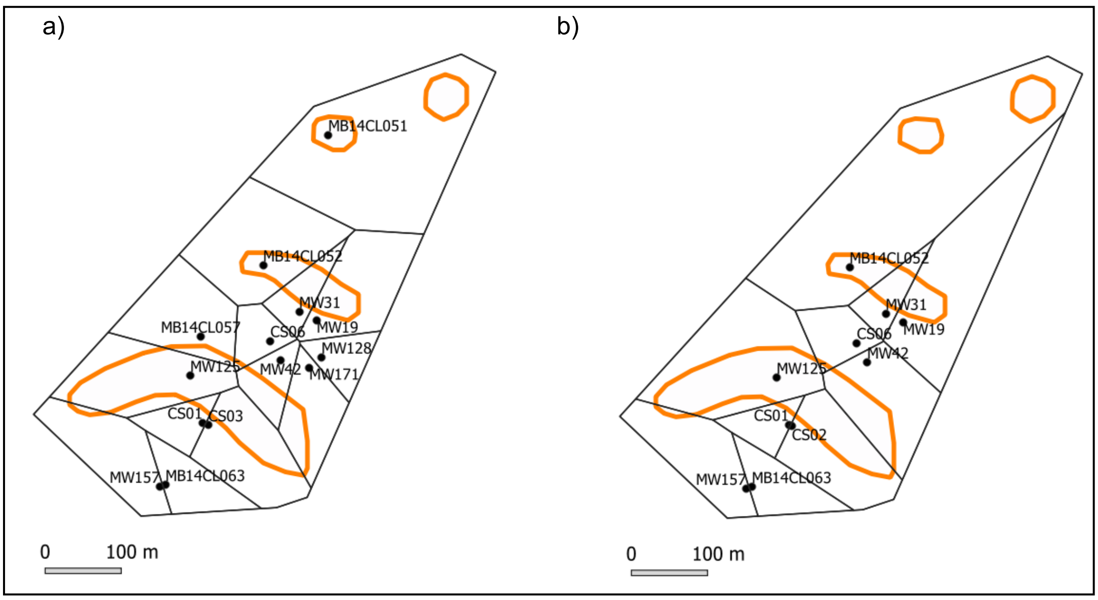


Figure E26: Voronoi polygon areas constructed using QGIS for thermistor measurement locations for (a) May 2019 and (b) September 2019. The inferred extent of LNAPL as of October 2017 is shown for reference (in orange).

NSZD rates determined using E-Flux methods were around 69 t/y. NSZD rates determined using temperature gradient methods were between 11 and 66 t/y. Rates from temperature gradient methods were more than three times greater in the dry season compared to the wet season.

Table E12: Tabulation of NSZD rates across methods used, and spatially weighted mass losses per time.

NSZD methods	**Intrinsic rate estimates** (L LNAPL ha^{-1} yr^{-1})*	**Rate mass/time** (t/yr) (weighted to the plume area)**
Soil surface CO_2 flux	• Traps: 1,100 – 10,000	• 69
Temperature:	• iButton strings: 5,200 (May 2019); 1,300 (Sept 2019) • Manual thermistors: 0–13,000 (May 2019); 0–3,600 (Sept 2019)	• 66 † (May 2019); 16 † (Sept 2019) • 35 (May 2019); 11 (Sept 2019)

*Assumed an LNAPL density of 703 kg/m³ (as octane); * Rates have been determined across a number of locations; the range denotes variability across different locations at the site. Values are rounded to 2 significant figures; ** A polygon areal weighting approach has been adopted to determine these rates, with the polygon areas scaled to the LNAPL plume area at the site (18 ha), except where noted (†).*

Comparison of active recovery and NSZD rates

The maximum long term LNAPL recovery rate from a range of remedial efforts was 3.8 t/y. By comparison, the NSZD rate was found to be in the order of three to 20 times larger than this maximum LNAPL recovery rate.

It must be noted that the site-wide NSZD rates have been calculated by different measurement techniques over two sampling campaigns at accessible locations. However, spatial representation of measurements over the 18-ha area may require some additional analysis due to the difficulty in accessing some areas due to heavy infrastructure and operations.

In addition, the stratigraphy at the site is complex with clays overlying highly weathered basalt and fresher basalt with different degrees of fracturing. Representing this profile with a single value for both thermal conductivity and gas diffusion coefficient was a necessary simplification due to the lack of data on these parameters. This introduces uncertainty along with the use of literature values. Seasonal variations at this site associated with water table elevations and changing soil moisture contents in the profile have a large influence on both active recovery and NSZD rates.

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